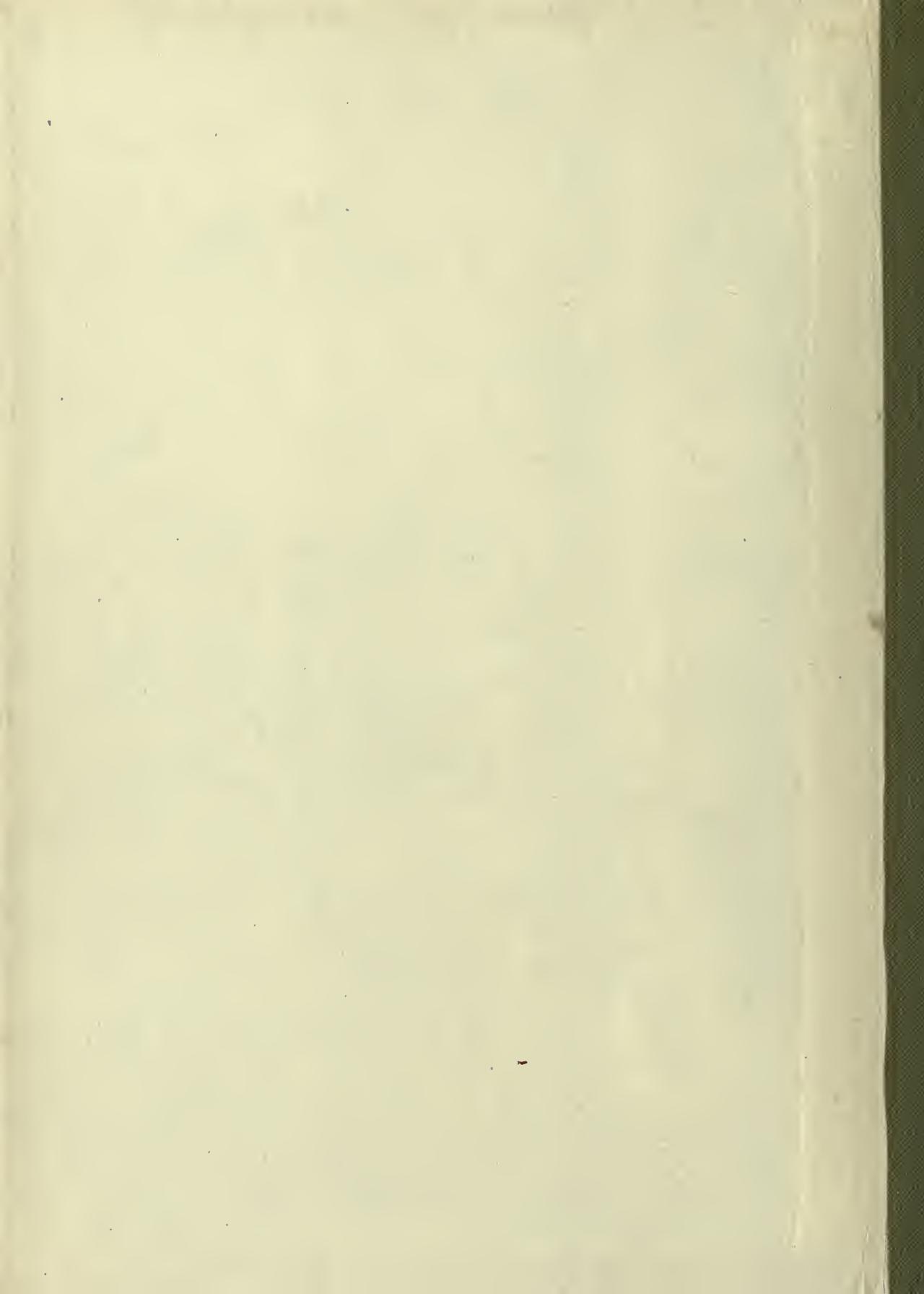
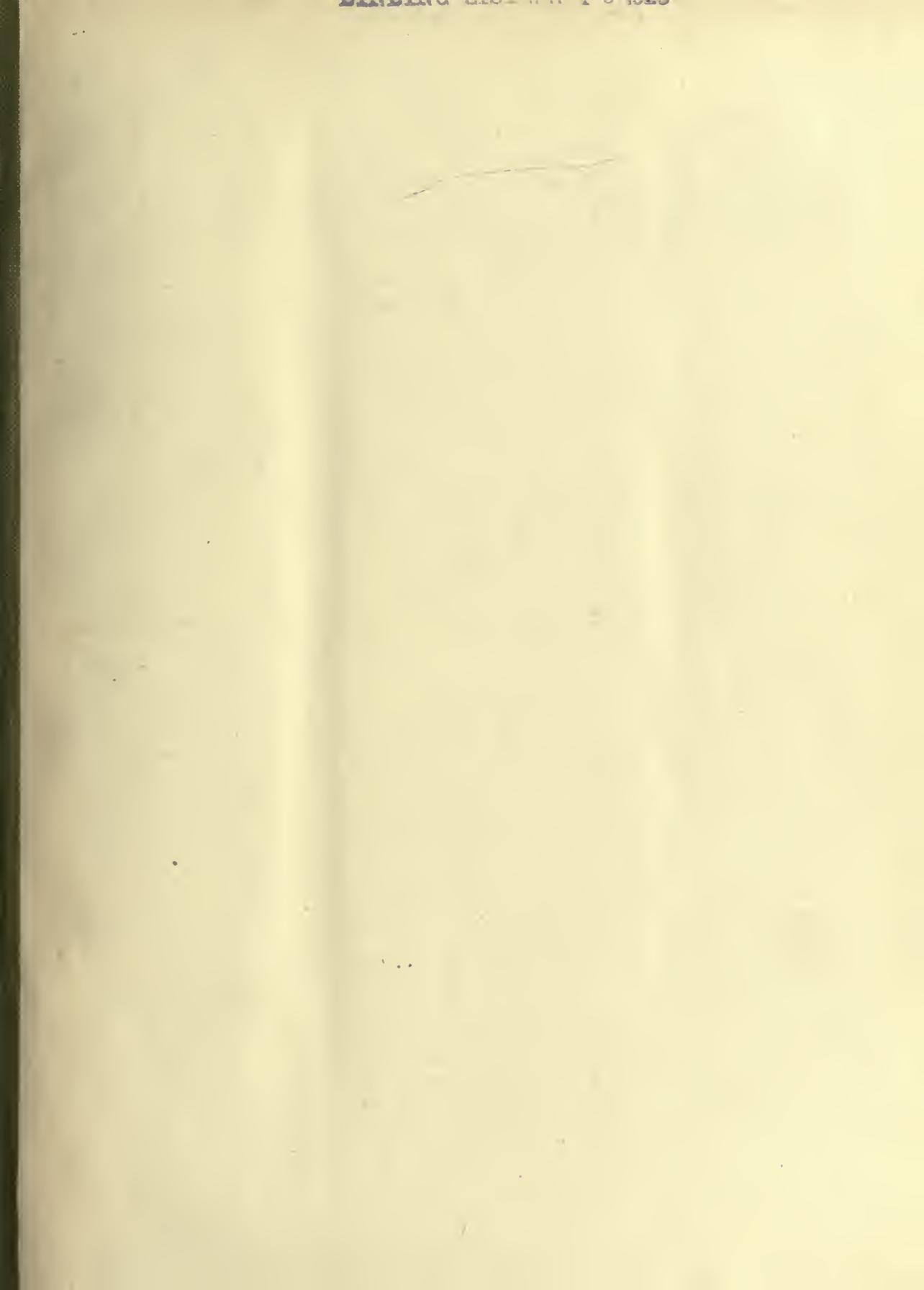


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# THE CHEMICAL NEWS,

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## A CONVENIENT METHOD FOR THE PREPARATION OF AQUEOUS HYDROBROMIC ACID OF CONSTANT BOILING POINT.

By J. G. F. DRUCE, M.Sc., A.I.C.

It is well known that when concentrated sulphuric acid is added to potassium bromide, the hydrobromic acid gas evolved is not pure, since the concentrated sulphuric acid exerts an oxidising action upon it, liberating some free bromine, and being partly reduced to sulphur dioxide.

Thus it is not possible to prepare pure hydrobromic acid by the interaction of sulphuric acid and potassium bromide unless a reducing agent of some kind is added to prevent the oxidation of the hydrogen bromide formed.

Pickles (*The Chemical News*, 1919, CXIX., 89) has described a very simple method for obtaining a strong aqueous solution of the acid free from bromine and sulphur dioxide by the distillation of a mixture of concentrated sulphuric acid (3.4 cc.) and potassium bromide (15 grams) dissolved in 25 cc. of water, to which a trace of stannous chloride (0.2 gram) has been added.

In repeating this work, it was found that a distillate began to come over at 103° C., and the temperature did not rise to 120° C. (the boiling point of the strongest solution of constant B.P.) until most of the aqueous hydrobromic acid had passed over. The distillation was also accompanied by much "bumping," which was not arrested by the introduction of pieces of broken glass or porous pot.

Much more satisfactory results were obtained by increasing the quantity of sulphuric acid to 10 cc., which was added to the 15 grams of potassium bromide dissolved in 25 cc. of water containing 0.2 gram of stannous chloride. The mixture was allowed to stand overnight, so that much potassium hydrogen sulphate crystallised out.

The supernatant liquid was decanted from the crystals and distilled. Nearly all the distillate came over at 120-125°. The temperature rose rapidly to 120°, and then very gradually to 125°, 18 cc. of distillate

were collected between these two temperatures.

In order to determine the exact yield of hydrobromic acid by this method, ten cc. of the distillate were made up to 250 cc. with distilled water, and quantities of 10 cc. were withdrawn and titrated with 0.2 normal potassium hydrate solution, using phenolphthalein as indicator.

It was found that 12.05 cc. of the alkali solution were required to neutralise 10 cc. of the diluted hydrobromic acid solution.

Thus this diluted acid contained 19.48 grams of hydrogen bromide per litre, and this indicates that the original distillate contained 48.7 per cent. of hydrobromic acid gas.

Since stannous chloride was used in the preparation of the hydrobromic acid, a trace of hydrochloric acid (not more than 0.07 gram) might be present in the product.

But disregarding this negligible amount, the yield of hydrobromic acid was thus over 90 per cent. of that which it is theoretically possible to obtain.

## MISSING ELEMENTS IN THE PERIODIC TABLE.

### PART III.

By F. H. Loring.

A study of the above subject (see *Chemical News*, Nov. 24, 1922, vol. CXXV., p. 309; and Dec. 29, vol. CXXV., p. 386) leads to some exceedingly interesting observations in connection with the relative quantitative production of the chemical elements. It will not be out of place, therefore, to discuss the matter further.

The existence of scandium in the sun, and it may be present there in considerable relative quantities, does not necessarily invalidate the view advanced, namely, that this element may not exist in relatively large quantities compared with that of its neighbours, because, according to recent speculations, the stars are manufacturing elements out of hydrogen, and any element, for example scandium, appearing in relative excess during the process of manufacture or element evolution, may not ultimately remain in the same quantities. The following quotation from Aston's book, "Isotopes" (1922), p. 103, bears upon this subject:—

"It has long been known that the chemical atomic weight of hydrogen was greater than one quarter of that of helium, but so long as fractional weights were general there was no particular need to explain this fact, nor could any definite conclusions be drawn from it. The results obtained by means of the mass-spectrograph remove all doubt on this point, and no matter whether the explanation is to be ascribed to packing or not, we may consider it absolutely certain that if hydrogen is transformed into helium a certain quantity of mass must be annihilated in the process. The cosmical importance of this conclusion is profound, and the possibilities it opens for the future very remarkable, greater in fact than any suggested before by science in the whole history of the human race.

"We know from Einstein's Theory of Relativity that mass and energy are interchangeable (Eddington, 'Time, Space and Gravitation,' p. 146), and that in C.G.S. units a mass  $m$  at rest may be expressed as a quantity of energy  $mc^2$ , where  $c$  is the velocity of light. Even in the case of the smallest mass this energy is enormous. The loss of mass when a single helium nucleus is formed from free protons and electrons amounts in energy to that acquired by a charge  $e$  falling through a potential of nearly thirty million volts. A swift  $\alpha$  ray has an energy of three to four million volts, so that the change of packing suggested by Brössler need not be nearly so great to provide the energy needed. If instead of considering single atoms we deal with quantities of matter in ordinary experience, the figures for the energy become prodigious.

"Take the case of one gramme atom of hydrogen, that is to say, the quantity of hydrogen in 9 cc. of water. If this is entirely transformed into helium the energy liberated will be

$$0.0077 \times 9 \times 10^{20} = 6.93 \times 10^{18} \text{ ergs.}$$

Expressed in terms of heat this is  $1.66 \times 10^{11}$  calories, or in terms of work, 200,000 kilowatt hours. We have here at least a source of energy sufficient to account for the heat of the sun (Eddington, *Brit. Assoc. address*, 1920; Perrin, *Scientia*, Nov., 1921). In this connection Eddington remarks that if only 10 per cent. of the total hydrogen on the sun were transformed into helium, enough energy would be liberated to maintain its present radiation for a thousand million years.

"Should the research worker of the future discover some means of releasing this energy in a form which could be employed, the human race will have at its command powers beyond the dreams of scientific fiction; but the remote possibility must always be considered that the energy once liberated will be completely uncontrollable, and by its intense violence detonate all the neighbouring substances. In this event the whole of the hydrogen on the earth might be transformed at once, and the success of the experiment published at large to the universe as a new star."

It is not quite clear how this energy cycle would work. When, for example, small quantities of  $H_2$  and  $O_2$  are exploded to form water ( $H_2O$ ) great heat is given out, but to explode water and get the energy back is impossible; for it is not given to us twice over. If the formation of the elements in the sun is due to the combination of protons and electrons taking place, how can we expect to get back heat already given away in the form of radiation? This is not probably the true interpretation of the above-quoted statement. It is assumed that if the hydrogen contained in the waters of the earth were united by some temperature and pressure condition as obtaining in the sun, the heat evolved would reduce the earth to a molten mass like the sun. However this may be, if this idea can be harmonised with radio-activity, it would be more acceptable; in which case one would have to assume that there are independent or free protons in the structure of the radio-element (very much as there are free electrons oscillating or revolving round a nuclear part), which combine explosively to form helium, but such explosions do not seem to extend to adjoining protons, for radio-activity is only concerned with a part of the whole atom—and therein, perhaps, lies our safety.

At one time it was roughly estimated that there were 50 million stars (suns). These, whatever their number may be, vary in size and temperature, so that the physical condition favourable to the production or degradation of different elements in varying quantities may also vary. Assuming that these at one time or another become most active in the production of elements, the quantitative production per star might vary considerably; in short, there would be many variables.

Other views than the above with regard to the origin of the excessive heat of the

sun have been advanced. Prof. Joly (*Nature*, 1922, vol. CX., p. 112) has recently suggested that the sun's heat is due to temperature and pressure effects stimulating radio-activity in practically all the elements favourably situated in this respect. This idea was discussed at considerable length in my "Atomic Theories" (1921), chapter XXI.

Sir Wm. Crookes' theory of the evolution of the elements is of interest in this connection. Quoting again from Aston's book, page 117, he says: "A more attractive theory than the one given above [that all the elements are the result of radio-active disintegrations, but these radio-changes were continued beyond the ordinary limit observed at present] is that the complex atoms of matter have been evolved by the aggregation of simpler atoms. This idea has received a good deal of attention in the past. Crookes (*Brit. Assoc. address*, 1886) remarks on it as follows:—'Let us picture the very beginnings of time, before geological ages, before the earth was thrown off from the central nucleus of molten fluid, before even the sun himself had consolidated from the original *protyle*. Let us still imagine that at this primal stage all was in an ultra-gaseous state, at a temperature inconceivably hotter than anything now existing in the visible universe; so high indeed that chemical atoms could not yet have been formed, being still far above their dissociation point. In so far as *protyle* is capable of radiating or reflecting light, this vast sea of incandescent mist, to an astronomer in a distant star, might have appeared as a nebula, showing in the spectroscope a few isolated lines, forecasts of hydrogen, carbon, and nitrogen spectra.

"But in due course of time some process akin to cooling, probably internal, reduces the temperature of the cosmic *protyle* to a point at which the first step in granulation takes place; matter as we know it comes into existence, and the atoms are formed.'"

"This vivid picture [of Crookes] may be brought up to date by substitution of free protons and electrons for the hypothetical *protyle*. We can imagine regions containing matter where the temperature is so high that not only is the dissociation of atoms from atoms and nuclei from planetary electrons complete, but also protons and electrons are in a state of agitation so violent that even the most stable nuclei cannot be formed. We should have here

matter of the simplest form we can imagine, or rather of no form at all, simply more or less neutral electric gas. Such a condition is by no means impossible in our universe and may actually occur during one of those excessively violent catastrophes occurring in far-distant space and observed by us as a new star.

"By some such cooling process as that suggested by Crookes we easily imagine the free charges combining to form the nuclei of elements. Whether those of heavier elements are formed direct by the charges getting into particular geometrical relations with each other, or whether helium nuclei are formed first and then subsequently coalesce depends on which theory of nuclear structure is adopted. In any case vast quantities of energy will have to be radiated off, and this radiation may be of such extremely high frequency that it is capable of disrupting nuclei themselves, so that there might be at this stage rapid and continuous transformations from heavier to lighter nuclei and *vice versa*.

"For the present we are interested in the number of each type of atom which survives. It is obvious that if the conditions of cooling are practically identical throughout the whole mass, there is no reason why the composition of the matter produced should vary. If 3 atoms of Cl<sup>35</sup> are formed to every 1 of Cl<sup>37</sup> at any one point, the same ratio must hold at every point so that a complex [composite] element of constant atomic weight will be formed. But it is much more likely that different parts of this primordial mass will undergo their transformations under different rates of cooling, etc., so it is worth while inquiring if variation in the mean atomic weight of a complex element is to be expected.

"The quantity of one particular atomic nucleus formed will probably depend (a) on the probability of a certain configuration of charges happening as a chance event; (b) the stability of the particular nucleus formed as the result of that event. Again, to take the case of chlorine, each isotope may be regarded as completely stable, and the relative quantities formed will simply depend on condition (a). Now it is not unreasonable to suppose that this is not seriously affected by different rates of cooling, and in this case the isotopes will be evolved in constant proportion. As we know of no natural process by which the proportion of isotopes can be altered appreciably, the complex elements will have to-

day the same chemical atomic weight as when they were first formed.

" . . . If the matter forming the earth went through a primordial stage such as that suggested above, it certainly did so more than  $10^9$  years ago. It follows that of the radio-active elements then formed, only two, thorium and uranium, will now be found on the earth, for the other radio-active elements existing to-day are of such a short period that they must have been formed since. Hence we may divide the *original* elements very simply and definitely into two groups: (1) All the stable; (2) Thorium and Uranium, whose nuclei are so complex that they are only partially stable."

This is all very interesting and more or less relevant to the subject under consideration; but, of course, extensive quotation widens the subject beyond the scope of the present argument. It is the aim, however, to punctuate these papers with interesting matter apart from the particularly novel features presented.

Problems of the kind involved in these studies are very difficult of proper solution, but converging lines of investigation often focus different observations into one common one, and thereby establish quantitative relations which can be accepted as being substantially true. It is important to keep in mind that each line of study may lead to some definite scientific or technical fact of permanent value, though at first it appears strange and contrary to common experience.

#### SUMMARY.

The existence of scandium in the sun does not necessarily invalidate any relative quantitative deduction as to the proportionate amounts of this element relative to that of those on each side of it in the atomic-number series, for the sun may be manufacturing or degrading practically all the existing elements, and any excess of one in particular may not appear in large relative quantities in the final state when this process of manufacture and degradation is finished. Quotations from Aston's book, "Isotopes," are given in general support of the argument. It is incidentally suggested that the danger of the hydrogen on the earth exploding to form helium, etc., is not probable; for if this theory be true in principle, then probably the energy of radio-changes, involving the expulsion of an alpha particle, is derived from the explosive combination of four protons to form helium; but, since other protons in the

atom are not exploded at the same time, the process is of a very prescribed nature—and therein perhaps lies our safety.

#### CORRECTIONS.

In Part I. of this series, p. 309, the bracket under VIII. should be extended to embrace the numbers 8, 9, and 10. In Periodic Table, same page, "S" should read "Si"; and the bracket at RaF should be turned the other way. On p. 310, left-hand column, 27th line from bottom of page, "Cs" should read "Rb." On p. 311, under Table III., "UX<sub>2</sub>" should read "UX<sub>2</sub>" for sake of uniformity.

#### THE COLOURING OF METALS.

A meeting of the Birmingham and Midland Section of the Society of Chemical Industry was held at the University of Birmingham, on Tuesday, Dec. 19, Dr. Maxted in the chair. There was a very large attendance of industrial chemists and metallurgists.

Mr. Alex. E. Tucker, F.I.C., read a paper on "The Colouring of Metals"—iron, steel, copper, and brass. He stated that with a given action of reagents, with or without external currents, the colour produced is a function of the time of the action. In speaking about the importance of current in bringing about the results, it will be admitted that all such actions where reagents affect the surface of the metal are in the ultimate meaning of the term, essentially electrical; in the process described, there is every indication of electrical cause and effect, though in one process external current is not used. The simplest illustration is that of the immersion of an iron or zinc surface in copper sulphate; copper is deposited. Again, if a piece of pickled zinc is immersed in a weak solution of copper tartrate and caustic soda, the colouring is slow, and may be arrested at any stage from a violet to steel blue, green, orange, yellow to purple red. Doubtless the action is entirely an electrical one, and the colour depends upon the thickness of the affected surface, but zinc castings may be bronzed by treating them with a mixture of ammonium chloride, potassium oxalate, and vinegar. Here, there is apparently no metal capable of being deposited, and the effect would appear to be due entirely to the altered sur-

face of the zinc and its consequent effect on vision. A considerable range of effects can also be obtained by heating metals to certain temperatures, thus obtaining a variety of coloured oxides, and this range may be extended if they are first coated with certain reagents, which need not necessarily be of metallic character. A cheap and extensively used method of blacking iron and steel goods is to heat them to a high temperature and to plunge them in oil. A superficial carbonising of the oil results, which for many purposes is quite satisfactory for rough articles; on the other hand, it is obvious that such heating is not permissible when hardness of surface is required. The process of blacking and tempering will not often go together, and the process is too crude. The well-known appearance of best gun bronzing is got by the rusting of the barrels, the ends being plugged; this rust is converted into the black oxide of iron by boiling the barrels in water through which air is passing; they are then mopped to remove the loose oxide, and they are again rusted and boiled. These processes are repeated many times in the best work, after which the work is oiled. The commoner bronzing of gun barrels is done with compounds of antimony. It is easy to produce fine effects by all colouring processes, provided the work is originally polished, indeed it is hopeless to treat any but the best surfaces—hence the common use of coloured varnish or even paint when such polishing is absent.

The author explained and gave demonstrations of new electrolytic processes—the Sentini Rondelli processes—in which no foreign metal is used for obtaining the colours, these depending on the alteration only of the surfaces of metals of which the goods are made. There are four processes in practical operation: (1) Dull black oxidising process, by means of which iron, steel, and cast iron parts may be oxidised a dull black. (This process, electrolytic in nature, also includes the derusting of iron, steel, and cast iron parts, and their preparation for enamelling, painting, etc.); (2) colour oxidising process, by which iron, steel, cast iron, and malleable iron parts may be oxidised in various colours, from an imitation of yellow brass to a dark brown colour; (3) copper on brass oxidising process, which is similar to process (1), but which provides for the oxidation of copper to a dull black, capable of being polished to a shiny black, and very resistant to chemi-

cal action; (4) the shiny black oxidising process, by which steel and cast iron parts may be oxidised to a brilliant black. (No current is required, and the oxidation is complete in a few minutes.) Acetylene welded tanks are used, as it is found that rivetted tanks will not stand the strong soda solutions and repeated heating and cooling. These tanks are heated by gas, and are electrically insulated in order to economise the heavy currents used.

Regarding to process (1), the author pointed out that the first requirement is to produce a sodium ferrite in the bath as the electrolyte. This may be readily formed by using a sheet of iron a little less in area than the long side of the bath as an anode in a caustic soda solution, and using a current of about 45 amps. for each square foot of the sheet; on reversing the current every few minutes for about an hour, a ferrite of soda is formed, and the bath is ready for production work. The progressive dissolution of the iron is shown by the reading of the voltmeter. At the beginning the voltage stops at a point under 1 volt for a very short time before reaching the stable value of about two volts. This is a direct reading of the polarisation phenomenon, and the intensity of this polarisation increases as the formation of the sodium ferrite increases. A good bath requires at a current density of 5 amps. per sq. dm. 2 or 3 minutes' depolarisation period. The colour and copper oxidising processes are simply variations of the conditions of working the above solutions. The shiny black oxidising process is entirely different, in that no current is used, the oxidation being effected by using an alkaline bath containing an oxide of a metal having electric negative behaviour relative to the iron, so as to produce oxidation of the iron surface with separation of the metal of the oxide used.

Mr. Tucker pointed out that the ferrites and ferrates of the alkalis may be regarded as compounds of the type  $\text{Na Fe O}_2$  or  $\text{Na}_2 \text{Fe}_2 \text{O}_4$ , in which the ferric oxide acts as an acid radical. The ferrate, on the other hand, is a name given to the compounds of the type  $\text{Na}_2 \text{FeO}_4$ , and which correspond to a ferric peroxide  $\text{FeO}_3$  and the hypothetical ferric acid  $\text{H}_2 \text{FeO}_4$ . It would appear that under the action of the powerful currents used, entirely different compounds must be formed; it would seem that the ferrite on which the processes depend corresponds to the formula  $\text{Na}_2 \text{FeO}_2$ ,

and is a white-greenish body not easily obtained in the solid state.

Although the surface produced on the iron articles is the magnetic oxide  $\text{Fe}_3\text{O}_4$ , and therefore is not capable of absorbing oxide, it is unfortunately too true that the articles treated are not entirely rustproof. It would appear that the surface, like nickel plating, is porous to damp and carbonic acid, and therefore in such atmospheres they will rust slightly. On the other hand, the surfaces are more resistant to rusting than any other process, with the exception of the old Bower Barff process, that he knew of. But that process depended on the formation of a thick coating of magnetic oxide—so thick that it was brittle and pealed. At the end of the depolarising period, the c.d. at the poles of the cell rises considerably, and this point coincides with the formation of a stable film of magnetic oxide on the electrode, the solution of iron ceasing on the reaching of the true surface of the electrode. There is, therefore, no corrosion. Magnetic oxide, as resulting from the action of the bath on the rust, is very easily reduced by cathodic reduction to metallic iron.

The time taken for the oxidising period to be completed depends upon the concentration of the ferrite in the bath and the length of the negative period, but as a rule it is in the vicinity of three minutes. The total time for the complete derusting and oxidising of an average steel part is 10 to 12 minutes. In general, all cast iron, malleable iron, steel, and wrought iron parts can be successfully oxidised. Special steels, such as some chromium and tungsten alloys, show a tendency to oxidise to a brownish-black tinge, and not to a deep flat black. This tendency can be overcome by the prolongation of the reducing and oxidising periods, and by increasing the current owing through the objects per sq. foot of area. The hardness of the coloured surfaces obtained is remarkable; they would stand any reasonable buffing, but not, of course, emery, etc.; the black oxide of copper surface is also remarkably hard, and is unaffected by sulphur from gas or rubber.

An interesting discussion followed, Professor T. Turner (Birmingham University), Dr. H. W. Brownsdon, Mr. Page (B.S.A. works), Mr. H. Silvester, and others taking part.

## COLLOIDS IN GEOLOGIC PROBLEMS.\*

By GEORGE D. HUBBARD.<sup>1</sup>

(Continued from Page 395).

### COLLOIDS AS CEMENTS.

It has long been known that nothing soluble occurs in the shales to hold them together, and yet they are extremely resistant to pulling strains. We say their tensile strength is high. The ultra clay in shales and clays has been shown by ceramists to consist largely of hydrated aluminium silicates, such as kaolin and halloysite, also nontronite, iron hydroxides, silicic acid, organic matter, and possibly aluminium hydroxide. These in their finely divided state are all colloidal, and as binders they are stronger when dry than Portland cement. They are the cement of shales and the strength of some limestones. Colloidal silica also serves as a binder in many sandstones. It is known, too, that the silica cements now in the crystalline state were deposited in some cases in chalcidonic or colloidal condition.

In addition to this colloidal material in the shales, it is known that opaline silica, when subjected to the processes of metamorphism, loses its  $\text{H}_2\text{O}$  and becomes crystalline quartz in a mica schist. Clarke<sup>13</sup> shows that colloidal matter contained in most muds and clays is perfectly capable of binding under the influence of pressure alone, and believes that shales owe most of their coherence to unions of this sort. He states on page 609 that it is possible for colloidal silica and colloidal hydroxides of aluminium and iron to react and form new silicates when the shales are metamorphosed into schists. Thus these finely divided materials play their parts in the make-up of metamorphic products derived from the shales.

\* From the *American Journal of Science*, August, 1922, p. 95.

<sup>1</sup> The author is deeply indebted at many points in the paper to Dr. Harry N. Holmes, of Oberlin College, for suggestions and criticism. His *General Chemistry and Colloid Manual* have been of much help also. This paper was presented to the Geologic Section of the Ohio Academy of Science, April 15, 1922.

<sup>13</sup> Clarke, F. W., *Data of Geochemistry*, U.S.G.S. Bull., MCXVI., p. 545.

This process must be closely akin to the one going on in the process of binding the materials of our stone roads. Grout<sup>14</sup> and Cushman<sup>15</sup> have been carrying on experiments on the cements of roads, and they think their work shows rather conclusively that the binding power of road-making materials is due to substances in the colloidal state, developed by hydrolyzing the oxides, probably of calcium, iron, and aluminium, thus making the body more or less plastic. Subsequently by crystallisation and dehydration they become firm, making a solid road.

#### ADSORPTION AND MINERAL COLOURS.

Very much can be said on the subject of adsorption and colloids which is not geologic, but a number of points certainly belong in this paper at this place. Every surface has an attraction for other substances. This holding-to a surface is called adsorption. Glue on a board or in a beaker adsorbs board or glass, that is, there is a strong attraction between the surface of the one and the particles of the other.

Adsorption, then, probably explains some of the colours of minerals, inasmuch as the particles of the mineral crystal correspond to the surface of the wood or glass, and the colouring is in such minute particles as to be in the colloidal state. Examples of such intimate relationships are found in the carbon and iron oxide which give the smoky tint to cairngorm, and the carbon which is believed to be responsible for the colour of amethyst. Rose quartz owes its colour to the adsorption of colloidal titanium on its particles as they come together to build up the crystal, and chrysoprase is said to be coloured much in the same way by nickel oxide. Feldspars have long been believed to owe their colour to traces of iron oxide which seems to be adsorbed by the molecules of the feldspar.

The beautiful blue colour of some halite has been shown to be due to metallic colloidal sodium, and probably the bluish tint of sylvite may be traced to the same cause. The colours of barite are thought by Patten to be due to various oxides. He has shown that it adsorbs salts of nickel, cobalt, cerium, iron and manganese. Calcite

is practically never a colloid, but it shows rather high adsorptive powers for certain colloids. The amber calcite has been shown to be due to organic matter, and the amber fluorite is probably due to hydrocarbons. Ruby spinel seems to owe its beautiful tints to adsorbed chromium oxide, and cerussite in blues and greens to colloidal hydrous copper carbonate. More than likely, though this is not demonstrated, the soft tints of the zinc salts, calamine, and smithsonite, from Laurium, Greece, are due to the adsorption also of copper carbonates. The colours of many gems may probably be due to adsorption of some finely divided substance which becomes so intimately mixed with the gem materials, yet which occurs in such minute quantities, as almost to defy detection. This problem has only recently been taken up, and we may, as the work goes on, find much more in it than has yet been shown.

#### COLLOIDS AND THE FLOTATION PROCESS.<sup>16</sup>

While the flotation process now practised in many of our ore concentration plants is not really a geologic problem, it is so closely connected with geologic materials that I venture to call attention to it here.

In the last few years, many of our large concentration plants have installed elaborate facilities for flotation of ores. By the use of this process, the heavy sulphides are separated from the gangue minerals in what might be called a reverse gravity method, because the heavy ores come to the top and are from there removed, while the lighter materials go to the bottom of the medium. But gravity has nothing to do with the process. If galena be wetted with water, and a drop of oil be put upon it, the oil displaces the water. Galena adsorbs oil much more strongly than it does water. On the other hand, if oil be spread over a quartz or calcite crystal and a drop of water be put upon it, the oil is at once displaced by the water. In other words, water is adsorbed much better by these common gangue minerals than is the oil.

For flotation the mineral is finely ground, usually in a wet condition, fine enough to pass through a 48-mesh sieve. A very small amount of pine, or some other oil with air is beaten into the water, which already contains the pulp of ore and gangue.

<sup>14</sup> Grout, F. E., *Journ. Am. Chem. Soc.*, 1906, XXVII., 1037.

<sup>15</sup> Cushman, A. S., *U.S. Dep. Agr., Bur. Chem., Bull.*, LXXXV., p. 92; *Trans. Am. Ceramic Soc.*, 1904, VI., 7.

<sup>16</sup> Moses, F. C., *Colloids and Flotation*, *U.S. Bur. Mines, Tech Paper CC* furnishes many data for this section.

The beating must not go far enough to make an emulsion or bring the oil into a colloidal state. The oily froth is made up of films of colloidal thickness, but is not emulsified. In this mixture the fine particles of sulphides adsorb the oil because it wets their surfaces, float to the top by means of their little coats, disperse themselves in the froth, and are scraped off the flotation tank. Then the froth is beaten out and the ore is free from most of the gangue which has, because wet by water, gone to the bottom of the flotation tank. More than 60,000,000 tons of sulphide ores are thus treated in the United States every year and carried much more cheaply to a higher concentration than was obtained by the old methods.

In the following ways, then, the subject of colloids touches the flotation process. The oil coat held by adsorption on the sulphides is so thin that the oil is really in colloidal state; in like manner, films of water of colloidal thickness wet or are adsorbed to the gangues. In a few cases colloidal kaolins and other clay substances are present, which interfere with the flotation, by adsorbing the oil and preventing its use by the sulphides. Here, too, the trouble increases if the oil is emulsified, for the finer the oil particles are, the more readily do the clay colloids adsorb them. Usually the ore is not ground fine enough so that its slime is at all colloidal. Electrolytes are sometimes used as an aid in flotation, for they help to prevent emulsions, or coagulate them if formed.

#### PLASTICITY IN CLAYS.

This subject has been the theme for many interesting papers, and of some heated discussions, but the air seems to be clearing, and Ashley<sup>17</sup> writes that it is pretty generally believed by the students of ceramics that the control of plasticity in clays is a matter of the control of colloids. A number of other writers can also be quoted in support of this position. A French ceramic chemist, T. Schlösing, in 1888, P. Rohland in various papers from 1902-9, A. S. Cushman, quoted above, and F. W. Clarke in the *Data of Geochemistry*, all agree that the plasticity of clays can be very directly traced to their colloid content. Schlösing shows, according to Ashley, that the amount of colloidal material in the best clays is small, and rarely exceeds one and

one-half per cent. As the percentage of material in the colloidal state decreases, so does the plasticity, and a clay with one-third of the amount mentioned is a lean clay. Likewise, if the amount is greatly increased above the one and one-half per cent., the clay becomes less plastic, and more sticky.

It is well known that the plasticity of clays is destroyed by ignition, and that the colloids are also made to change state by the same treatment. On the other hand, many thoroughly ignited clays absorb water quite as well as unignited ones. This makes it clear that the colloidal material is not the cause of the absorption of water, nor is the absorption of water vitally related to plasticity. Series of experiments have been made with lean clays to increase their plasticity, and it has been found that very poor clays can be made plastic enough to be worked successfully by adding small quantities of certain colloids; agar-agar 0.08 per cent. increases the plasticity of different clays as much as 40 and in some cases 60 per cent., and aluminium cream produced the same effects by adding in much larger quantities, *e.g.*, about 3 per cent.

As was shown on a previous page, colloidal material increases the tensile strength of shales, and it has been shown to do the same for clays. Other colloidal substances have also been used to increase the plasticity. Humus, for example, an organic colloid, produces beneficial results in lean clays. Clays in a cool, moist place improve in plasticity even within a few weeks. It is believed that the development of organic matter in the clay by the growth of bacteria, or even protozoa, is responsible for the improvement, for the protoplasm of these minute organisms is itself a colloid.

If plasticity of clays should be found to be dependent upon the inorganic colloids in them, it might be pertinent to ask if clays and shales laid in the sea would be more plastic than those laid in fresh water, where the finest or colloidal material had difficulty in being precipitated.

Ries<sup>18</sup> has shown that the fineness of the material, the thinness of the plates in the shale, and the colloids, are each in themselves inefficient to fully explain plasticity. His theory suggests that plasticity may be due to cohesion and adhesion factors which depend on the constitution of the molecule,

<sup>17</sup> Ashley, H. E., *Bur. Stand., Tech. Paper*, 1911, XXIII.

<sup>18</sup> Ries, H., *Geol. Survey, W. Va.*, 1905, vol. III., pp. 46-54.



but not on the chemical composition. It might be said that he does not seem to be fully satisfied with his explanation, for he adds that "practical work to improve the plasticity of clays may follow lines already started, such as the addition of colloids, and weathering, which may mean the addition of colloidal material by bacterial growth."

One can never understand the raw materials and their relations to the finished products in cements, brick and terra-cotta, pottery, porcelain, enamels, and glass, until he has dipped rather seriously into the study of colloids from the geologic side. Weathering is a colloid-producing process, as well as a maker of most of the soils and the salts of the sea. Since macadam, brick, cement, and asphalt roads all start with materials whose vital properties are connected with the colloidal state of matter and the geologic processes that produce these materials, the road industry has real need of a colloid geologist.

#### COLLOIDS IN SOILS.

Perhaps this topic will take us as far into questions of physiography as the last has into metallurgical and industrial processes, but in the last analysis, all three go straight back to geologic processes, and involve geologic problems. Soils result from the normal geologic decay of rocks, primarily of silicate rocks. In their decay, the elements K, Na, Ca, and Mg usually go into true solution in their secondary salts, while silica, aluminium, and iron go chiefly into colloidal solution and constitute the ultra-clay material of clays and shales.

In solutions, the colloidal material can be separated from the crystalline material by the use of the Sharples' centrifugal machine, capable of producing a force seventeen thousand times that of gravity, or by the use of the Pasteur-Chamberland filter. This separation can also be brought about by coagulation by the addition of salts, and by dialysis.

In soils the body is essentially sand and clay, the sand being made of fragments of many kinds of minerals, but mostly of quartz; and the clays mostly of hydrous aluminium silicates, with smaller quantities of aluminium and iron hydroxides. When the salts mentioned above come to the soils they are carried on through, providing the water has free circulation and drainage below; but if there is insufficient rainfall to equal evaporation, then these salts may be

left in the soils and be continually carried to the surface by evaporation of the water. The colloidal material, however, will usually be adsorbed and will remain in the soil. Too much of the latter tends to clog a soil and prevent the free and necessary movement of air and water.

This last item becomes particularly troublesome in soils that must be irrigated, for irrigation waters differ from rain waters in carrying both true solution and colloidal solution materials, thus furnishing more material to clog the soil than rain waters. The difficulty is still further increased by the fact that most of the water on irrigated lands is removed by evaporation, so that everything of both kinds of solution is left in the soil. The colloids become a nuisance usually much before the salts do when ordinary stream water is used for irrigation. The colloids tend to cement the soil together some little distance below the surface, usually not beyond the reach of the plough, and produce there a "hard pan" layer. This interferes with the movement of the water, either up or down, and of course prevents the roots striking deeply. It can be broken up by deep cultivation, but the soil experts are now of the opinion that treatment with an electrolyte is really better. Aluminium sulphate has been successfully used in a number of cases. It acts much as the salts do in the sea, by coagulation of the colloidal material into little pellets, large enough so that the water and the air can get among them, and thus prevents their operation as cements.

In western United States, where most of our irrigation is carried on, there have been discovered in recent years great quantities of aluminium sulphate, and it is believed that a large use of this salt will greatly extend the life of our irrigated soils.

The subject of colloids in geology is just beginning to attract the attention of men who should be concerned with it. While the chemists have tackled their colloid problems with vigour and enthusiasm, the geologists have all but neglected the whole field. There should be many geologists turning their attention seriously to the solution of the great numbers of problems now before us, such as these suggested in this paper, and there should be many more geologists keeping up with the literature that discusses these colloid problems.

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## PROCEEDINGS OF SOCIETIES.

## PHYSICAL SOCIETY OF LONDON.

PROCEEDINGS AT THE MEETING HELD ON  
DECEMBER 8, 1922, AT THE IMPERIAL  
COLLEGE OF SCIENCE.

*Alexander Russell, M.A., D.Sc., in the  
Chair.*

1. A paper on "*The Relation between Molecular and Crystal Symmetry as shown by X-ray Crystal Analysis*," was read by MR. G. SHEARER, M.A., B.Sc.

## ABSTRACT.

The methods of X-ray analysis enable the number of molecules associated with the unit cell to be determined. With the help of this information an attempt is made to connect the symmetry properties of the crystal with this number and with the symmetry properties of the molecules from which the crystal is formed.

The symmetry number for each of the 32 crystal classes is given, and is shown to mean the minimum number of asymmetric molecules necessary in the unit cell to satisfy the symmetry conditions. The relative orientations and positions of these molecules in the cell are discussed.

It is suggested that this symmetry number is the actual number of molecules in the cell when the molecule is asymmetric; further that, if the molecule possesses symmetry, this symmetry appears also in the crystal, and the number of molecules in the unit cell is obtained by dividing the symmetry number of the crystal by the symmetry number of the molecule.

Evidence is produced in support of these hypotheses and examples are given of their application to inorganic and organic crystals.

## DISCUSSION.

The President, before calling on Sir William Bragg, congratulated him in the name of the Society on the honour recently conferred upon him by the Paris Academy of Sciences.

Sir William Bragg, after acknowledging the congratulations tendered to him, said that the paper before the meeting was an important one, throwing a new light on the possibilities of investigating crystal structure. The Author's intricate but lucid argument affords a great simplification of the

problem. Three unitary structures have to be considered: (1) The chemical molecule, as it exists in solution; (2) the elementary crystal lattice or cell, consisting of groups of (3) crystal molecules, in which the atoms and electrons are not necessarily arranged in the same manner as in chemical molecules. The author's method enables one to determine the symmetry of these groups at once from the geometry of the crystal, with a very little help from X-rays. A considerable vista of research is thus opened up, which may serve to settle such questions as that of the static versus the dynamic model of the atom.

Dr. J. W. Evans thought that the methods employed by Mr. Shearer gave promise of proving of great assistance in working out the structure of crystals. There were, however, some considerations that must not be neglected:

(1) It is by no means certain that molecules always maintain their identity in the crystalline state.

(2) Even where they exist in the crystal, they may not retain the same form and symmetry as in a free state.

(3) Although in an ideal crystal all the cells are identical, and have identical orientation, this is by no means always actually true. We know that cells of different composition may be employed indiscriminately if they are approximately the same in form and volume, as in the case of the plagioclase feldspars.

In the same way, if the outer forms of cells of the same substance approximate to a higher symmetry than the cell itself, these cells may, even when differently orientated, be employed in building up a crystal structure. The same may be true with cells that are enantiomorphically related. In these cases the whole structure may have a higher symmetry than the individual cells as the result of either (a) a symmetrical arrangement of the cells in the nature of molecular or ultramicroscopic twinning—twinning is usually an attempt to attain higher symmetry—thus forming lattice cells of greater size; or (b) indiscriminate occurrence of cells differing in orientation or in enantiomorphic character. In the former case it might be very difficult to recognise by means of X-ray analysis the primary cells. In the latter case it would, I should think, be impossible.

The explanation of the crystalline structure of potassium chloride is not convincing. The symmetry of the molecules shown is that of the quartz or tri-

gonal trapezohedral class which is represented by the symbol IIIUh (J. W. Evans, *Min. Mag.*, Vol. XV., pp. 398-400, 1919), with three digonal axes at right angles to a trigonal axis, and making angles of  $120^\circ$  with each other; whereas that of the crystal structure is stated to belong to the cuprite or pentagonal eikositetrahedral, CUh class, in which there are four trigonal axes corresponding to the diagonals of the cube and three digonal axes at right angles to one another and parallel to the edges of the cube. The cell contains four molecules, and the trigonal axes of these are supposed by the author to be at right angles to the diagonals of the cube, but it is not explained how the  $4 \times 3$  digonal axes at right angles to the diagonals are transformed into three digonal axes at right angles to one another.

From the examination of the material prepared at the Imperial College and a comparison of the work of other observers, Miss Knaggs, of the Imperial and Birkbeck Colleges, has shown that the symmetry of the crystal structures of the simpler carbon compounds frequently bear close relation to that of the molecule. Substances of the type  $CX_4$ , where X is an element, are usually cubic. Those of the types  $CX_3Y$  are trigonal or hexagonal, unless X is hydrogen, when the symmetry is lower. Those of the form  $C(CX_3)_4$  are as a rule cubic, and those with  $C(CX_2Y)_4$  are tetragonal. In all cases the symmetry is apt to be that of a higher or different class than would have been expected, though one belonging to the same system. In the case of the  $C(CX_2Y)_4$  compounds the symmetry of the molecule would be that of chalcopyrite or tetragonal scalenohedral, IVBk class, whereas that of the crystal usually belongs to the IVBc, or in one case IVBu class. It can be shown that symmetry of this character would be obtained by appropriate molecular twinning. Some of the compounds considered are dimorphic, reystals with less symmetry forming at a lower temperature.

The Speaker threw out the suggestion that crystal structure might possibly be due to the repulsion of the electrons of different atoms combined with an attraction of the atoms as a whole. If it be supposed that, contrary to the usual view, there are six outer electrons in chlorine having their mean position arranged like the points of an octahedron, and that in potassium there are eight electrons arranged like the points of a cube, it will be evident that a position of stability would be obtained when the

points of each chlorine octahedron were opposite the centres of faces of the surrounding potassium cubes and the points of each potassium cube were opposite the centre of a face of a chlorine octahedron, and that the potassiums and chlorines would then be arranged alternately in a cubic lattice just as we know to be the case.

The author's reply will be communicated later.

2. A paper on a "*Modification of the Powder Method of Determining the Structure of Metal Crystals.*" by E. A. OWEN, M.A., D.Sc., and G. D. PRESTON, B.A., was read by Mr. Preston.

#### ABSTRACT.

Plates of aluminium, iron, copper, lead and magnesium have been examined by means of the Bragg X-ray spectrometer, employing radiation direct from a molybdenum anti-cathode. The maxima observed in the spectra are sufficiently intense to measure with accuracy, and the crystalline structure of the materials examined are readily determined. A few of the results obtained by the method are included in the paper as typical examples.

#### DISCUSSION.

Sir William Bragg congratulated the authors on their work, which indicated that the technique of crystal analysis is improving, and that its methods are coming into general use. A consideration to be borne in mind is that one of the crystal planes may become unduly accentuated by the polishing process. Further, in the case of aluminium and other metals, it is possible for individual crystals to be very large.

Dr. G. D. West, after dwelling on the advantages of focussing the X-ray beam by inclining the plane in which the crystals lie, inquired as to the width of the slits employed as the conditions varied, and as to the allowance to be made for variations in the output of the bulb.

Mr. Preston, in reply, stated that the authors had been careful to use crystals less than 1 mm. in size. The chamber slit was kept at 2 mm., and the bulb slit varied from 2 mm. to 4 mm. for different parts of the spectrum. The output of the bulb could be kept constant by regulating the filament current, but for moderate accuracy little regulation was required.

3. A paper on "The Cathode Ray Oscillograph," by A. B. Wood, D.Sc., was read by Capt. C. S. Wright.

#### ABSTRACT

The paper deals with a new form of cathode-ray oscillograph adapted for commercial production and laboratory use. The instrument described is of the low-voltage type, in which a hot cathode is employed as a source of the electron current. This low-voltage type of oscillograph is much more sensitive than the high-voltage cold-cathode type designed by M. Dufour. Various methods are described for focussing the cathode-ray stream, and a proposal has been made for an oscillograph with external (*i.e.*, outside the vacuum) photographic film. Experiments have been made to determine the most suitable photographic film or plate. Ordinary gelatine-coated roll films or plates are unsuitable, owing to the marked absorption of the cathode-rays by the gelatine. The best results have been obtained with Schumann plates containing a proportion of calcium tungstate. This material phosphoresces with a light rich in ultra-violet, and consequently the secondary luminous effect on the Schumann plate is very great.

Mechanical, electrostatic and electromagnetic methods are described for generating a time-axis on the records. For certain purposes this time axis is sinusoidal, whilst for others it is linear. Numerous records of high-frequency A.C. wave forms and of impulsive electrical phenomena have been obtained, and a few of these are reproduced in the paper. Brief reference is made in conclusion to the applications of the oscillograph to research and electrical engineering problems, where other well-known forms of oscillograph (Duddell, Einthoven, &c., types) cannot be employed on account of the inertia of the moving element.

#### DISCUSSION.

Mr. Mines inquired whether any measurement had been made of the potential gradient in the tube with a view to determining the distribution of potential along the path of the rays. Was anything known of the current density of the rays, and was there (as in the arc lamp) a limiting value to such current density, involving a maximum intensity for the spot of light beyond which it would be impossible to go? And had the author tried the focussing effect of charging the cylindrical shield to a potential of, say, 100 volts?

Mr. R. A. Watson Watt (partly communicated): I would join in congratulating Dr. Wood on his very lucid account of a most important and valuable instrument of research. Perhaps the most outstanding feature of his work is the way in which the oscillograph has been converted into a robust engineering structure, which the "glass shy" engineer can approach with more confidence than he feels towards the older forms of blown glass tube, and into an instrument with a much higher expectation of life than these older forms possessed.

In considering cathode ray oscillographs in general, one should not lose sight of the fact that there is a wide field of application for sensitive tubes in which it is not necessary to resort to photography with its attendant difficulties and complications. Single axis working, in which the tube is valuable as a direct reading high-frequency voltmeter, is in itself sufficient justification for such tubes. But Dufour has shown that in wave form work one can obtain visual images of radio frequency wave forms from his high-voltage tubes, while recently, by the courtesy of the International Western Electric Co., I have been able to satisfy myself that a reliable visual image of a transient deflection of  $10^{-4}$  sec. duration can be obtained with the 300-volt beam of their tube. The fluorescent spot had a translational speed of about  $5 \times 10^{-4}$  cm. per sec. in this experiment. This, whether due to persistence of vision or to persistence of fluorescence, is much more satisfactory than one had the right, *a priori*, to expect.

On minor matters of detail it might be desirable in a paper which will take an important place in the chronology of cathode ray oscillographs that the author should make it clear that he does not assign priority for the introduction of the hot cathode, of the A.C. time base, and of the D.C. time base, to the workers referred to in this paper. The author's own familiarity with the history of the subject might lead to the appearance of neglecting the priority of Wehnelt (1906) as to the hot cathode, of Fleming (1913) as to the A.C. time base, and of Dufour (1914) as to the D.C. time base, which he superposed on the A.C. base, so that the final image is based on the plane projection of a cylindrical helix.

I should be grateful if Dr. Wood could say whether any data are available as to a tube working on the 100 volts, which he mentions as a lower limit. A tube of this extreme sensitivity would be most valuable,

but I know of no references to a stably operating tube with an accelerating voltage below 300 volts.

Finally, I should like to ask the author whether he has any experience of Van der Bijl's "positive ion" method of focussing, as used in the Western Electric tube. It appears to be a method of great value, particularly in view of the fact that the commonly used electro-magnetic "paralleling" method reduces the sensitivity of the tube. My experience of low-voltage tubes leads me to conclude that at the present moment the limitation of sensitivity for visual observation lies, not in the mechanism of beam production or concentration, but in the fluorescent materials used for the screen, and that progress in that direction can still be made.

Mr. R. S. Whipple said that the beautiful instrument described would meet a real demand, as oscillographs using a cold cathode are cumbersome and costly, while the one under discussion should be within the means of most laboratories. The method of phosphorescent sensitisation opens up great possibilities. The paper is written in such a way as to be unusually readable.

The reply to the discussion will be communicated later.

4. *A DEMONSTRATION of a Low Voltage Cathode Ray Oscillograph* was given by Mr. R. WEBB, International Western Electric Company.

This instrument, which is designed to work at 300 volts, is intended for manufacture on a commercial basis. The cathode consists of a hot platinum filament coated with cerium oxides, and formed into a circle coaxial with the path of the rays. It is protected from bombardment by positive rays, which would disintegrate it, by a screen in which is cut a circular hole slightly less in diameter than the filament. It has a life of about 200 hours. The anode is a platinum tube through which the rays pass. The deflecting fields are electrostatic, and are provided by two pairs of plates at right angles. The bulb is in the form of a conical flask, the cathode being at the narrow end so that the rays impinge on the flat bottom which is coated inside with fluorescent matter. The luminous trace of the rays can be seen from outside through the bottom of the flask. The apparatus was connected up\* to show the characteristic of an oscillation-generating valve, so that the potential difference be-

tween one pair of plates was proportional to the grid potential, and that between the other pair to the plate current. The resulting trace consisted of a single curved line terminating in a loop of peculiar form at one end.

\* *E. V. Appleton, Phil. Mag., August, 1921.*

The Annual Exhibition of Apparatus arranged by the Optical Society and the Physical Society of London, was held on January 3rd and 4th, 1923.

The following lectures were given:—

"*Reproduction of Colour by Photographic Processes*," by MR. W. GAMBLE (on January 3 at 4 p.m., and January 4 at 8 p.m.).

"*Recent Photo-Elastic Researches on Engineering Problems*," by PROF. E. G. COKER, F.R.S. (on January 3 at 8 p.m., and January 4 at 4 p.m.).

#### PLATINUM DEPOSITS.\*

By James M. Hill.

The Salt Chuck palladium-copper mine in Alaska was not operated in 1921, though one shipment of concentrates produced in 1920 was sent to the United States. The output of placer platinum came mainly from Dime Creek, on Seward Peninsula.

California dredges produced practically all the crude platinum reported for 1921, a total of 821 ounces. Of this quantity 486 ounces came from the streams of the mother lode region, and 335 ounces from Trinity County. A large part of the Trinity County crude platinum is osmiridium, recovered from Beegum and Hayfork creeks and by the dredges on Trinity River.

A large part of the 91 ounces of crude platinum reported by Oregon miners was produced at the beach mines in Coos and Curry counties, though some crude platinum was saved from the mines near Kerby and Waldo, in Josephine County, and near Sumpter, in Baker County.

The Electrolytic (formerly Rambler) mine, near Holmes, Albany County, Wyo., was under development during the year, and a car of ore was shipped principally for its copper value.

A number of platinum booms were launched in 1921, notably one based on reports of rich platinum ore 11 miles from Winnemucca, Nev., and another on a reported deposit of platinum near Batesville, Ark.

#### CANADA.

The largest production of platinum metals in Canada comes from the refiners of the Sudbury nickel-copper ores. The International Nickel Co. closed its mines and refinery September 1, 1921. The Mould Co. is the only one now operating.

#### COLOMBIA.

Two dredges of the South American Gold and Platinum Co. were in operation in Colombia throughout the year, and a third dredge was expected to be in operation early in 1922. The boat of the British Platinum and Gold Corporation is reported to have made satisfactory recovery,<sup>1</sup> the output from December 21, 1920, to May 21, 1921, being 966 ounces. A dredge has been ordered by the newly organised Colombia Proprietary Gold Mines (Ltd.), a British concern, to operate on Ilantin River, 70 miles south of Buenaventura. It is stated on good authority that the native production of platinum decreased considerably during 1921, owing to the lower price paid for the metal by local buyers, which naturally was reduced in conformity with the New York market. It is believed that the production may decline somewhat from that maintained during the war period for a few years, until sufficient dredges are installed to handle adequately the large reserves of gravel.

#### PAPUA.

The first recorded shipment of osmiridium from Papua was made in 1921 and amounted to 88 ounces. Australians evidently believe that the east end of New Guinea may yet prove a mining field for this valuable iridium-osmium alloy.

#### RUSSIA.

Very little real news concerning the situation in the Russian platinum fields has been forthcoming. Apparently a little hand mining is going on. Late in 1921 it was reported that a State-controlled platinum trust had been organised by the Soviet Government, and in May, 1922, it was reported that Louis Duparc<sup>2</sup> is going to Russia to reorganise the platinum-mining industry at the invitation of the Soviet Government.

It is reported<sup>3</sup> that the production of platinum during the first half of 1921 was about 2,700 ounces.

#### TASMANIA.

The production of osmiridium in Tasmania in 1921 was 1,750 ounces, as compared with 2,009 ounces in 1920, 1,670 ounces in 1919, and 1,607 ounces in 1918. This is rather surprising in view of the fact that the prices paid for the alloy have been continually lowered until it was reported that many miners had abandoned operations. An excellent description of the various fields in Tasmania in which osmiridium is mined is that by Reid,<sup>4</sup> published in 1921.

\* By James M. Hill. *Mineral Resources of the United States, 1921—Part I. Government Printing Office, Washington, 1922.*

<sup>1</sup> *Min. Jour. (London)*, 1921, vol. XXV., p. 50.

<sup>2</sup> *Eng. and Min. Jour.-Press*, 1922, vol. CXIII., No. 18, p. 786.

<sup>3</sup> *Note by Dept. Commerce of a translation from Economic Life.*

<sup>4</sup> Reid, M. A., *Osmiridium in Tasmania: Tasmania Geol. Survey Bull* 32, 1921.

## A PRELIMINARY STUDY OF ZIRKITE ORE.

By J. G. THOMPSON.

(From the *Journal of Physical Chemistry, New York, December, 1922.*)

This investigation consists of a study of zirkite ore (crude zirconium oxide), with attempts to improve the refractory properties by the elimination of certain of the impurities present in the raw material.

Pure zirconium oxide, if available in sufficient quantity, would aid materially in solving the problems of the users of high-temperature refractories, particularly those problems connected with the extreme temperatures encountered in the use of the electric furnace. As a refractory for high temperatures zirconium oxide is far superior to any of the materials commonly employed for this purpose, and in some respects it approaches the ideal refractory. It possesses<sup>1</sup> a melting point higher than that

<sup>1</sup> Meyer: *Met. Chem. Eng.*, 1914, XII., 791; 1915, XIII., 263; Hedvall: *Zeit. anorg. Chem.*, 1915, XCIII., 313; Bradford: *Chem. Trade Jour.*, 1918, LXII., 284; Arnold: *Jour. Soc. Chem. Ind.*, 1918, XXXVII., 724; Granger: *Chem. News*, 1919, CXVIII., 115, 121.

of any other known metallic oxide; it is non-volatile below its melting-point; it is neutral in character and inert to the action of practically all of the common reagents; it possesses low coefficients of thermal and electrical conductivity. These properties ensure the successful use of pure zirconium oxide as a refractory, even for the most extreme service conditions, at any time when it becomes available in quantity.

(To be Continued.)

### GENERAL NOTES.

#### INTERVIEWS WITH HIS MAJESTY'S COMMERCIAL SECRETARY IN ARGENTINA.

Mr. H. O. Chalkley, His Majesty's Commercial Secretary at Buenos Aires, will be in attendance at the Department of Overseas Trade for a few days, from January 18, 1923, and will be pleased to interview manufacturers and merchants interested in trade with Argentina.

Applications for interviews should be made as soon as possible, and in any case not later than January 17, to the Comptroller-General, Department of Overseas Trade, 35, Old Queen Street, London, S.W.1, the reference, T.G.4380, being quoted in all cases.

Department of Overseas Trade.

#### BOARD OF TRADE ANNOUNCEMENT. SAFEGUARDING OF INDUSTRIES ACT—PART I. ARBITRATIONS UNDER SECTION 1 (5).

##### *Oxalic Acid.*

Judgment has been given by the Referee in the matter of a complaint under the above sub-section, that Oxalic Acid has been improperly included in the lists of articles chargeable with duty under Part I. of the Act. The Referee has awarded that the complaint fails, and the lists therefore remain unaltered.

Board of Trade,

20th December, 1922.

### NOTICES OF BOOKS.

*Smith's Intermediate Chemistry*, revised and rewritten by JAMES KENDALL

and EDWIN E. SLOSSON. Pp. XV. + 566 + 16 plates. For Great Britain: G. Bell & Sons, Ltd., Portugal St., Kingsway, W.C. 1922. Price 8s. 6d.

Alexander Smith's *Chemistry* bears the stamp of much originality, and was written by one possessed of great teaching qualities. Although in some respects the book was not perfect, it undoubtedly was a very good textbook.

The present edition has been extensively revised and brought well up to date by Profs. Kendall and Slosson. It is eminently suitable for students in colleges and technical institutes, and also for those who do not regard chemistry as their principal subject.

Besides the usual textbook features there is much interesting and apposite information upon matters usually ignored in such works as this, which are intended to maintain and retain the students' live interest in the subject.

Extensive additions to the earlier edition have been made to incorporate the latest information concerning Atomic Energy and Structure. The subject matter is frequently treated from the viewpoint of physical chemistry. The importance of this in the study of general chemistry is justly emphasised.

The Introduction, "Why Study Chemistry?" makes very refreshing reading. It is pointed out that chemistry began as a secret science. The early chemists concealed their knowledge (and their ignorance) under mystic symbols. The modern chemist, on the other hand, is more anxious to explain what he knows than people are to listen to him.

Chemistry is well fitted to give training in the scientific method, since it is *experimental*. Properly taught — or properly learned — it inculcates self-reliance and independence of thought. Further, the qualified chemist has two strings to his bow. If he does not like teaching, he may enter the industrial field. He may be engaged in routine analysis of raw and finished products, or be in control of processes, or engaged in research to utilise waste products, or to invent new compounds or new uses.

In some fields of Chemistry, women have almost an equal chance with men.

Chemistry should have an interest and utility for everyone. J.G.F.D.

*The Mysteries of Hypnosis (Les Mys-*

tères de l'Hypnose), by GEORGES DE DUBOR, translated by G. M. HORT. Pp. IX. + 235. London: William Rider & Son, Ltd., 8, Paternoster Row, E.C.4. 1922. Price 5s. net.

It is regrettable that psychical phenomena have been exploited, in the past, by charlatans, and consequently their study has been discredited. Happily, this stage is rapidly passing, particularly in view of the number of eminent scientists who have witnessed and investigated these phenomena, and who vouch for their authenticity.

This interesting scientific and authoritative treatise upon Hypnosis can be safely recommended to those desirous of ascertaining the facts and phenomena concerning this subject.

The author has been careful to select fully authenticated cases, and has included those instances which are most striking and illustrate his contentions. J.G.F.D.

#### BOOKS RECEIVED.

*Smith's Intermediate Chemistry*, revised and rewritten by JAMES KENDALL and EDWIN E. SLOSSON. Pp. XV. + 566. 1922. New York: The Century Co. Sold in Great Britain by Messrs. G. Bell & Sons, Ltd., Portugal Street, Kingsway, W.C.2. 8s. 6d. net.

*The Theory of Emulsions and Emulsification*, by WILLIAM CLAYTON, D.Sc. (LIVERPOOL), F.I.C., Foreword by PROFESSOR F. G. DONNAN, C.B.E., M.A., &c. Pp. VI. + 160. 1923. Messrs. J. & A. Churchill, 7, Great Marlborough Street, W.1. 9s. 6d. net.

*Bleaching Powder and its Action in Bleaching*, Original Memoirs by R. L. TAYLOR, F.I.C. Pp. 78. 1922. Messrs. John Heywood, Ltd., 121, Deansgate, Manchester. 4s. 6d.



This list is specially compiled for the *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

#### Latest Patent Applications.

33109—Harris, H.—Separation of arsenic and tin in presence or absence of antimony. Dec. 4.  
33075—Hirschberg, L. M.—Extraction of sulphur and sulphur compounds. Dec. 4.  
33605—Williams, J. G.—Manufacture of low relative density oxide and carbonates of magnesium. Dec. 8.

#### Specifications Published this Week.

163047—Nitrogen Corporation.—Process of prepar-

ing mixtures of nitrogen and hydrogen such as are suitable for the production of ammonia.

- 167156—Man, W.—Manufacture of concentrated hydrogen peroxide solution  
188772—Wolverkamp, M. E.—Salts of oxidised protalbinic and lysalbinic acids.  
188811—Deutsche Gold & Silber-Scheideanstalt vorm. Roessler an. Schaidlauf, Dr. A.—Process of bleaching textile fibres.  
188815—General Electric Co., Ltd.—Apparatus for transforming the crystal structure of wires, filaments, and the like.  
177972—L'Air Liquide Soc. Anon. Pour L'Etude et l'Exploitation des Procédes, G., Claude.—Synthesis of ammonia.  
188933—British Dyestuffs Corporation, Ltd. and Wyler, M.—Manufacture of phenyl gly-cine compounds.  
172944—Aktieselskabet Labrador.—Precipitation of iron in mineral acid alumina solutions.  
189160—Gitsham, J., and Evershed, H. R.—Process for the manufacture of sulphate of lead.  
189193—Wake, J. F.—Rotary apparatus for drying, calcining, or roasting ores, low temperature distillation of fuel, and apparatus for similar purposes.  
181375—Aktieselskabet de Norske Saltverker.—Process of producing anhydrous magnesium chloride.  
185403—Farbwerke vorm. Meister Lucius & Bruning.—Manufacture of thiohydrius.

#### Abstract Published this Week.

*Manures; Ammonium Salts; Ammonia*.—Patent No. 187251.—Some improvements in processes for obtaining artificial manures have been devised by Mr. E. L. Pease, of Harworth Moor, Darlington, County Durham.

Manures containing an ammonium compound or compounds and a secondary fertilising agent or agents, such as a salt of potassium or a phosphate, are obtained by reaction between gases containing ammonia and the semi-dry product obtained by treating with acid a naturally-occurring material that contains the secondary fertilising agent or agents, but which is free, or almost free, from lime, and is not generally regarded as a manure in itself. Thus clay containing a compound of potassium may be treated with sulphuric acid, if desired, after drying and pulverising in sufficient amount to constitute a semi-dry mass, which is brought into contact with gases containing ammonia. The product contains the oxides of iron and aluminium, and ammonium sulphate, together with a soluble compound of potassium, the content of which may be increased by direct addition of potassium salts. Other examples of naturally-occurring materials, suitable for use in the process, are alunite and shales containing iron aluminium, sulphur and potash, with or without phosphorus. Alunite may be calcined and used without any addition of acid. Instead of sulphuric acid there may be used sulphur dioxide or trioxide, hydrochloric or phosphoric acid, spent pickling-liquor, or acid salts, or mixtures of any of these. Where phosphoric acid is used, gases containing ammonia may be treated in a heated condition: if, however, the absorption is allowed to proceed for a long time at atmospheric temperature, material containing tri-ammonium phosphate is obtained. The products may be lixiviated to remove the soluble salts, or they may be heated to about 400° C., when about 50 per cent. of the ammonia present is evolved, leaving a residue still suitable for use as a fertiliser or for re-use in the process. Alternatively the ammonia may be expelled by means of lime.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the official price of 1s. each.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3274.

## THE BRITISH EMPIRE EXHIBITION (1924).

### THE CHEMICALS SECTION.

Arrangements have now been completed for organising on a very large scale the Chemicals Section of the British Empire Exhibition. The organisation of the Section has been entrusted to the Association of British Chemical Manufacturers, whose Committee will be reinforced by representatives of the Society of Chemical Industries and kindred bodies connected with the Chemical Industry and Science. The work of letting space is now proceeding, 25,000 sq. ft. having been allotted to the Chemical Section.

Mr. W. J. Woolcock, of 116, Piccadilly, is acting as Secretary, and there is every indication that the exhibit will be one fully worthy of the great Chemical Industry. In fact, it may be said that this section stands next to the engineering, electrical, and transport sections of the Exhibition in the satisfactory demand for space. A large number of the big manufacturing firms of the kingdom have already applied. It is probable that a portion of the section will be devoted to perfumery. Suggestions have also been received from firms desiring to show the whole process of toilet soap making by modern machinery, with shaving and toilet soaps of all descriptions, dentifrice, and other toilet preparations.

### THE ESTIMATION OF MAGNESIUM IN ALUMINIUM ALLOYS.

By W. H. WITHEY, B.A. (CANTAB.), OF THE  
NATIONAL PHYSICAL LABORATORY.

The increasing use of magnesium in aluminium alloys containing several metals has complicated the analysis of such alloys, and any method by which it can be shortened without loss of accuracy is very much to be desired.

In a paper read before the Institute of Metals in 1916, the author published details of a method in which use was made of the fact that tartaric acid prevents the precipitation of iron and aluminium by ammonia, but at the same time does not

prevent the estimation of magnesium as phosphate even in the presence of a large quantity of aluminium.

In the process as originally devised, metals such as zinc, copper, nickel, iron, and any others which could be separated by sulphuretted hydrogen, were removed prior to determining the magnesium as phosphate. This necessarily lengthened the process, since it prevented the estimation of the magnesium in a separate portion.

As a result of experiments it has now been shown that it is not necessary to remove metals such as zinc, copper, nickel and iron (if present in only small amounts), and that the accuracy in the subsequent determination of the magnesium is quite as high as when the metals are absent. The method has been tested, as regards accuracy, by adding a definite amount of magnesium to solutions of aluminium containing copper, zinc, and nickel, in proportions which are not likely to be exceeded in practice, and then estimating the amount of magnesium present. The figures thus obtained agree very closely indeed with those found in the same amount of the pure magnesium solution. The details as given below for the test experiments are applicable to the analysis of aluminium alloys not containing more than 1 per cent. of magnesium, the amount of alloy used for the analysis being 2 gms. To obtain successful results the conditions must be carefully observed, particular care being taken to see that the solution is *very distinctly* alkaline before the addition of the sodium phosphate, otherwise there is a risk of contaminating the magnesia precipitate with some of the heavy metallic phosphate. If, on addition of the sodium phosphate, a precipitate is produced immediately, more ammonia should be added, when it will be found that the precipitate redissolves, and that only after some time does the magnesia commence to come down.

For the purpose of the tests, a very impure aluminium (Si 0.36, Fe 1.50, Cu 0.65) was chosen, and several portions of 2 gms. dissolved in a mixture of 30 cc. hydrochloric acid, 10 cc. nitric acid. This was followed by evaporation to dryness after the addition of 15 cc. sulphuric acid. The dried mass was dissolved in water, and the silica removed by filtration. To each of these solutions was added 15 gms. of tartaric acid dissolved in 75 cc. water, 5 gms. ammonium chloride and 5 cc. of a stand-

ard solution of magnesium sulphate. The metal whose action was to be investigated was added in the form of a standard solution, and one metal only was used for each separate test.

The solutions as thus prepared were next treated with strong ammonia (s.g. 0.830) until they were *very distinctly* alkaline, 40 cc. was found to be sufficient for the purpose. Twenty-five cubic centimetres of a saturated solution of sodium phosphate were then added and the liquids vigorously stirred, and more ammonia added until it formed at least one-third of the total volume, which should be about 400 cc. After allowing to stand overnight, the solutions were filtered, washed with dilute ammonia, and then dissolved in hydrochloric acid, and precipitated again in the presence of 1 cc. of a saturated solution of sodium phosphate, as in the case of pure magnesium in solutions.

When the precipitates had settled for several hours, they were again filtered,

washed as before, and ignited. In the case of alloys containing manganese it will usually be found that the magnesium precipitate contains a portion of the manganese. The ignited precipitate should, therefore, be dissolved in nitric acid s.g. 1.2, cooled, treated with sodium bismuthate, filtered and titrated with ferrous ammonium sulphate, and any manganese thus found calculated as  $Mn_2P_2O_7$  and deducted from the weight of the impure phosphate.

Any traces of calcium present in the alloy would also probably be precipitated, but as a rule calcium is only likely to be introduced by means of the magnesium used in making the alloys, the actual amount of calcium is likely to be very small indeed, and for any but the most accurate analyses could be ignored. In certain cases where calcium is added intentionally, although in small amounts, a modification of the process may be necessary.

#### EXPERIMENTAL RESULTS<sup>o</sup>

Weights of metals present.

Al	Fe	Cu	Zn	Ni	$Mg_2P_2O_7$ found	Mg Calculated
nil	nil	nil	nil	nil	0.0568	0.0124
2.0000	0.0300		nil	nil	0.0562	0.0125
2.0000	0.0300	0.1000	nil	nil	0.0566	0.0124
2.0000	0.0300	0.5000	nil	nil	0.0570	0.0125
2.0000	0.0300		0.2278	nil	0.0580	0.0127
2.0000	0.0300	nil	0.4556	nil	0.0604	0.0129
2.0000	0.0300	nil	nil	0.2000*	0.0562+	0.0123
2.0000	0.0300	nil	nil	0.4000*	0.0552+	0.0121

+ In these cases pure metallic nickel was used, dissolved in aqua-regia.

\* In the first experiments made with nickel a sample of nickel ammonium sulphate was used, which proved to be contaminated with magnesium. 1 gm. of the salt was added to one solution and 2 gms. to the other. The weights of precipitates obtained were 0.0714, 0.0838; on treating some of the nickel salt alone in the presence of tartaric acid and phosphate 2 gms. gave 0.302, which amount of  $Mg_2P_2O_7$  was also obtained after separating all other metals previous to precipitating the phosphate. Making the corrections for the magnesium in the nickel salt, the amounts corrected should have been 0.0563 and 0.0536, corresponding with 0.0123 and 0.0118 Mg.

The method has also been tried on two alloys of a fairly complex type, which on analysis by decomposing with caustic soda and subsequent determination of the metals seriatim, gave

	1	2
Si .....	0.22	0.22
Cu .....	2.29	3.91
Mn .....	0.58	nil
Mg .....	0.61	1.56
Zn .....	19.10	nil
Ni .....	nil	1.93

After removal of the silica and applying the tartaric method as above, the magnesium found was respectively 0.59 per cent. and 1.54 per cent., as against 0.61 and 1.56.

The precipitates obtained in the first series of experiments were also examined for possible contamination, by dissolving them in dilute hydrochloric acid followed by careful neutralisation, addition of sodium acetate and dilute acetic acid. The slight precipitate was redissolved, and reprecipitated, and on ignition was proved to

be a minute quantity of ferric phosphate which was without significance in the result. It should also be pointed out that with the exception of the filtrate from the magnesium phosphate solution obtained from the copper solution, only a faint darkening, but no precipitate, with sulphuretted hydrogen could be obtained. The method may, therefore, be regarded as reliable, and is more expeditious than the older methods, as it enables the magnesium to be estimated on a separate portion of the alloy.

### LEGAL INTELLIGENCE.

#### RICHMOND POLICE COURT.

##### ARSENIC IN COCOA.\*

##### *Summons Under Sale of Foods and Drugs Act, 1875.*

At the instance of the Surrey County Council, on December 18, 1922, the Home and Colonial Stores, Ltd., were summoned for "selling at their George Street shop, Richmond, to the prejudice of Robert Alfred Houghton (county inspector), the purchaser, cocoa which was not of the nature, substance, and quality of the article demanded by such purchaser, but was adulterated with arsenic (arsenious oxide) to the extent of one-fortieth of a grain per pound of cocoa, contrary to Section 6 of the Sale of Foods and Drugs Act, 1875." Messrs. Rowntree and Co., Ltd., Cocoa Works, Haxby Road, York, were summoned for aiding and abetting in the commission of the alleged offence by the Home and Colonial Stores, Ltd.

The Mayor (Alderman P. E. Metzner) presided over the Bench. Mr. R. O. B. Lane (instructed by the Surrey County Council) prosecuted; Mrs. Travers Humphreys appeared for Messrs. Rowntree; and Mr. W. Ricketts appeared for the Home and Colonial Stores, Ltd.

Both defendants put in a formal plea of "Guilty."

Mr. Lane, for the prosecution, said the summonses were taken out by Mr. Houghton, an inspector of the Surrey County Council. On October 2 Mr. Emery, an assistant to Mr. Houghton, went to the Home and Colonial Stores, Richmond, and asked for a quarter of a pound of cocoa. He was served with a packet from under the counter, for which he paid 4½d. It was

marked, "Home and Colonial pure cocoa essence, highest-grade quality, guaranteed absolutely pure cocoa." He was informed that the cocoa in question was not the actual manufacture of the Home and Colonial Stores, but a blend of seven different cocoas, one of which was manufactured by Messrs. Rowntree. Samples of the seven different cocoas were given to Mr. Emery, and when Messrs. Rowntree's sample was analysed, it was found to contain arsenic to the extent of one-tenth of a grain per pound. He wanted to say at once, and acting on his instructions, that he did not suggest that the Home and Colonial Stores were really to be blamed in the matter. There had been a breach of the law, but he did not think it could be said that there was any moral culpability attaching to them; but the law had to be carried out.

Mr. Edward Hinks, analyst to the Surrey County Council, said that he analysed a sample of cocoa in which he discovered arsenic to the extent of one-fortieth of a grain per pound. The quantity was excessive. On November 14 he received further samples of cocoa, and with regard to one marked "Rowntree" he found it to contain arsenic to the extent of one-tenth of a grain to a pound of cocoa. The other samples he found to be genuine. In reply to Mr. Travers Humphreys, who asked him if he suggested that anyone was in the least likely to be injured in health by the use of the cocoa containing one-tenth of a grain per pound, witness said he thought it was on the line where it might be harmful. He had not heard of anyone being harmed by it.

Mr. Travers Humphreys said Messrs. Rowntree took absolute responsibility for the position in which the Home and Colonial Stores had been placed. They bought from Messrs. Rowntree what they believed to be pure cocoa. Messrs. Rowntree were most anxious that two matters should be put clearly before the Bench. They desired first to put before the public through the Bench that in the opinion of the most competent scientific men there was not the smallest cause for anxiety as to illness or danger to the public from drinking the cocoa which was the subject of the prosecution. The other matter was that this was an accident which might have happened to any manufacturer of any article of food, in spite of the greatest possible care being taken to prevent impurities being present. In July last there was brought

to the notice of Messrs. Rowntree by some chemist that some of the loose cocoa supplied contained some faint traces of arsenic. The news came like a thunderbolt to the firm. Their chemists were put on double shifts, working day and night. Everything in the place was analysed, and for some time there was not the faintest notion where the arsenic could have come from. It was found that the impurity was in the alkali carbonate of potash, which had been used by Messrs. Rowntree for years. It was used in small quantities to make the cocoa soluble and more digestible. They got it from the best people in the trade. They found it contained a substantial quantity of arsenic, and they wrote to the manufacturers about it, but so far had not received any explanation. There was one thing they could do, and they did it instantly—they sacrificed the whole of the cocoa, 350 tons, representing many thousands of pounds, sacrificed it absolutely in order that nothing more might go out of their works. They then instituted a new test, and they were able to say with absolute certainty that as from August 1 every ounce of cocoa from their works was made from ingredients absolutely free from this impurity. There was on the market somewhere the amount of cocoa they had sent out containing this impure carbonate of potash. They first ascertained if it could do any harm. The view of the chemists was that the amount of arsenic present could not possibly injure anyone in health who consumed it. They considered whether it was possible to get back the cocoa they had sent out to the trade, but decided it was absolutely useless to try to get it back, because they had 65,000 customers, many of them wholesalers. The period during which the impure cocoa was sent out was only two months in all. Messrs. Rowntree came to the conclusion honestly that it was in the interests of the public not to create a quite unjustifiable scare in connection with such a valuable article of food as cocoa. He wished to emphasise that chocolates did not come into the matter in the least. Chocolates were made from cocoa which contained no addition of the carbonate of potash.

Mr. Arnold Rowntree said his firm had never spared any expense in regard to analysing articles of food. With regard to the incident, witness said the whole of the stock was sacrificed, amounting to about 300 tons, varying in value from £100 to £520 a ton.

Mr. Ricketts, on behalf of the Home and Colonial Stores, said they purchased the cocoa with a warranty from Messrs. Rowntree. Directly they heard that the cocoa contained impurity they withdrew sixty-five tons from their shops and twenty tons from their warehouses, involving them in a loss of £12,000.

A fine of 40s. was imposed against the Home and Colonial Stores, and £20 against Messrs. Rowntree, with 50 guineas costs.

\* From the "Pharmaceutical Journal and Pharmacist," December 23rd, 1922.

#### THE TEMPERATURE COEFFICIENT OF THE REFRACTIVE INDEX OF AMERICAN TURPENTINE.

By GARTHA THOMPSON (B.Sc., F.I.C.).

It is a remarkable fact that while it is generally recognised that it is impossible to compare refractive indices unless these refer to the same temperature, few attempts have been made to measure and record the variation of the refractive index with temperature. This is specially true of commercial liquids. Hence, there have been demands by analysts that all workers should adhere to a standard temperature when measuring refractive indices. The better way, however, is to ascertain both the refractive index and its temperature coefficient (*i.e.*, the decrease in refractive index per degree Centigrade), for then a small calculation is all that is necessary to reduce refractive indices to any desired temperature. The advantage of being able to calculate the refractive index for any temperature when its value is known at one temperature is obvious.

It is a fortunate fact, from this standpoint, that while liquids of analogous chemical constitution vary in their refractive indices, the temperature coefficients of these refractive indices remain fairly constant; and it is an equally fortunate fact, from another standpoint (*viz.*, that of differentiating between substances of dissimilar chemical constitution), that while the refractive indices are often the same at one temperature, yet the temperature coefficients of the refractive indices vary widely. In fact, where dissimilar liquids are concerned, it is frequently found that there are far wider differences in the temperature coefficients of the refractive indices than in those constants themselves.

As is the case with many other liquids, the temperature coefficient of the refractive index of turpentine appears to have been neglected. The only information which could be found on this subject is given in Kanthack's "Refractive Indices of Essential Oils" (Adam Hilger, Ltd.). Here the temperature coefficient of the refractive index of American turpentine is given as 0.00037, and it may be remarked that this figure is so low as to be quite outside the usual range of essential oils. It was therefore decided to carry out a series of tests, using the best commercial varieties of American turpentine.

The samples of turpentine numbered 1, 3, and 4 were described as "Genuine Commercially refined Spirits of American Turpentine"; sample 2 was described as "best American Turpentine."

A Pulfrich refractometer constructed and recently calibrated by Messrs. Adam Hilger, Ltd., was used for the work, and temperature control was maintained by allowing a stream of water at the desired temperature to flow through the jackets enclosing the prism and cell and through the heater which was inserted in the turpentine in the cell. A sodium flame was used as illuminant throughout the experiments.

From the third columns in the tables it will be seen that there is little, if any, tendency for the temperature coefficient to alter with temperature.

All four samples of turpentine were examined chemically; for the figures in table 4 (with the exception of those for the second sample) I am indebted to the Routine Section of the Laboratories.

In conclusion, I desire to express my thanks to the Directors and Chief Chemist (Mr. W. B. Parker, F.I.C.), of the British Thomson-Houston Company, Ltd., for permission to use the research laboratories for this work.

TABLE 1. SAMPLE 1.

Temperature	Refractive Index.	Temperature Coefficient.
14.2° C.	1.474428	0.0004672
20.5	1.471486	0.0004663
32.1	1.466076	0.0004723
39.2	1.462722	0.0004633
48.0	1.458644	0.0004732
57.4	1.454197	Mean 0.0004684

TABLE 2. SAMPLE 2.

Temperature	Refractive Index.	Temperature Coefficient.
20.0° C.	1.469902	0.0004675
30.0	1.465227	0.0004719
45.0	1.458163	0.0004705
60.0	1.451110	Mean 0.0004696

TABLE 3. SAMPLE 3.

Temperature	Refractive Index.	Temperature Coefficient.
15.5° C.	1.472804	0.0004677
30.0	1.466022	0.0004735
50.0	1.456552	Mean 0.0004706

TABLE 4. SAMPLE 4.

Temperature	Refractive Index.	Temperature Coefficient.
15.5° C.	1.472853	0.0004711
30.0	1.466022	0.0004685
50.0	1.456652	Mean 0.0004698

TABLE 5.

Sample No.	Specific Gravity 15.5° C	Iodine Value.* 24 hours Hüpl	1st drop	Below 155° C	Distillation.			
					155° C to 165° C	Below 175° C	Below 185° C	Above 185° C
1	0.8679	423.1	152° C	0.05%	95.0%	96.5%	97.0%	3.0%
2	0.8724	407.3	153° C	2.05%	90.0%	93.0%	96.0%	4.0%
3	0.8705	399.2	155° C	—	93.0%	95.5%	96.0%	4.0%
4	0.8707	396.0	154° C	0.05%	92.0%	94.0%	95.0%	5.0%

\* 150% excess iodine was used.

PROCEEDINGS AND NOTICES OF  
SOCIETIES.

ROYAL SOCIETY OF ARTS,

JOHN STREET, ADELPHI, LONDON, W.C.2.  
169TH SESSION, 1922-23.

Arrangements for Meetings during  
January, 1923.

Wednesday, Jan. 17th, 8 p.m. (Ordinary Meeting): C. A. KLEIN, *Hygienic Methods in Painting—the Damp Rubbing Down Process*. T. M. Legge, C.B.E., M.D., will preside.

Friday, Jan. 19th, 4.30 p.m. (Indian Section): THE EARL OF RONALDSHAY, G.C.I.E. (late Governor of Bengal), *A Clash of Ideals as a Cause of Indian Unrest*. The Right Hon. Viscount Peel, G.B.E., Secretary of State for India, will preside.

Wednesday, Jan. 24th, 8 p.m.: SIR WILLIAM HENRY BRAGG, K.B.E., D.Sc., F.R.S. (Quain Professor of Physics, University of London), *The New Method of Crystal Analysis, and their Bearing on Pure and Applied Science*. "Trueman Wood" Lecture. Alan A. Campbell Swinton, F.R.S., late Chairman of the Council, will preside.

Wednesday, Jan. 31st, 8 p.m. (Ordinary Meeting): THOMAS H. FAIRBROTHER, M.Sc., F.I.C., and ARNOLD RENSHAW, M.D., D.P.H., *The relation between Chemical and Antiseptic Action in the Coal Tar Dyes*.

THE FARADAY SOCIETY.

ORDINARY MEETING, MONDAY, JANUARY 15,  
1923, AT 8 P.M.

At the Chemical Society, Burlington  
House, Piccadilly, W.1.

Papers to be read:—

E. W. J. MARDLES: *The Scattering of Light by Organosols and Gels of Cellulose Acetate*.

*Study of the Reversible Sol to Gel Transition in Non-Aqueous Systems*.

I. *The Change of Viscosity with Time during Gelation*.

II. *Viscosity Changes associated with the Gel to Sol Transition*.

*Changes of Volume and Refractive Index associated with (a) The Formation of Organosols and Gels. (b) The Reversible sol to gel Transition*.

PROF. J. R. PARTINGTON and W. G. SHILLING: *The Variation of the Specific Heat of Air with Temperature*.

PROF. A. W. PORTER and J. J. HEDGES: *The Law of Distribution of Particles in Colloidal Suspensions, with Special Reference to Perrin's Investigations*. Part II.

SOCIETY OF PUBLIC ANALYSTS AND  
OTHER ANALYTICAL CHEMISTS.

1st January, 1923.

MEETING AT NOTTINGHAM.

A Joint Meeting of the Society, with the Nottingham Section of the Society of Chemical Industry, will be held at the University College, Nottingham, on Wednesday, January 17th, at 7.15 p.m.

The chair will be taken by the Chairman of the Nottingham Section of the Society of Chemical Industry, Mr. S. F. Burford, F.I.C.

A general discussion on: *The Detection and Determination of Small Quantities of Arsenic*, will be opened by Mr. A. Chaston Chapman, F.R.S., President of the Institute of Chemistry.

Mr. J. M. Wilkie will read a paper on the subject, and among those taking part in the discussion will be: Mr. S. R. Trotman, Mr. H. Droop Richmond, and Dr. G. W. Monier-Williams. The Chairman will call upon further speakers by name, and those desiring to contribute to the discussion should communicate with the Honorary Secretary.

Apparatus for the electrolytic determination of arsenic will be exhibited by Dr. G. W. Monier-Williams and Mr. J. M. Wilkie.

In order to promote a free discussion, the meeting will be private, and closed to the Press, but an official summary will be issued subsequently.

MINERALOGICAL SOCIETY.

TUESDAY, JANUARY 9, AT 5.30.

A. BRAMMALL and H. F. HARWOOD: *Dartmoor Granite, (a) Rutile, Brookite and Anatase: Genesis; (b) Varieties of Zircon: their significance*.

DR. A. HUTCHINSON: *A graphical method of correcting specific gravity determinations*.

DR. L. J. SPENCER (with microscopical determinations by W. CAMPBELL SMITH, and chemical analyses by E. D. MOUNTAIN): *A davyne-like mineral and its pseudomorphs from St. John's Island, Egypt*.

We have been asked to make known that the membership of the American Chemical Society is open to members of any of the recognised English chemical societies.

Forms for membership and full particulars will be sent on application to the Secretary, American Chemical Society, 1,709, G. Street, N.W. Washington D.C., U.S.A.

#### BOOKS RECEIVED.

*Formulary of the Parisian Perfumier*, by R. M. GATTEFOSSE. Pp. 82. 1st English Edition. 1923. La Parfumerie Moderne, 19, Rue Camille, Lyon.

*Cements and Artificial Stone* (a descriptive Catalogue of the specimens in the Sedgwick Museum, Cambridge), by JOHN WATSON (late) Hon. M.A., F.G.S. Pp. XII. + 131. 1922. W. Heffer & Sons, Ltd., Cambridge. 6s. net.

#### A PRELIMINARY STUDY OF ZIRKITE ORE.

By J. G. THOMPSON.

(From the *Journal of Physical Chemistry*, New York, December, 1922.)

(Continued from Page 15.)

Zirconium was discovered by Klaproth in 1789; but, for many years after its discovery, it was considered one of the rare earths, and occasional samples of zircon, the orthosilicate of zirconium, were the only sources of supply. At present deposits of zircon sands, usually associated with monazite sands, are known to exist in many localities, but the deposits usually are of limited extent and the zircon content is small. Zirconium also occurs in small amounts in a number of rare ores, but these are important only for the traces of radio-active elements which they contain. Present interest centres solely upon the oxide ores of zirconium generally known as "Baddeleyite" ores. This group includes a number of ores of indefinite and variable composition in which the zirconium oxide content varies up to 99 per cent. The name "Zirkite" has been restricted to the baddeleyite ore from the huge Brazilian deposits which now supply practically all of the demand for zirconium. Zirkite ore is variable in composition, but careful sorting at the mine furnishes a pro-

duct which is fairly uniform in composition averaging about 80 per cent. zirconium oxide. It is stated<sup>2</sup> that an unlimited supply of this ore is available, as the deposits are of vast extent. The only factors limiting the output are the difficulties due to primitive methods of mining and transportation.

The use of zirconium oxide always has depended upon its refractory properties; but this use, until recently, was confined to the small amounts of very pure material required for the incandescent element in the Nernst, Drummond, and Bleriot lamps; as an additional element mixed with the thoria and ceria in Welsbach mantles; etc. The discovery of the huge Brazilian deposits of high-grade ore has awakened much interest in the possibility of using this ore on a large scale as a refractory.

Many of the properties of the raw ore<sup>3</sup> are comparable with those of the pure oxide, but the melting point (2,950°-3,000° C. for Pure ZrO<sub>2</sub>) drops to 1,200°-2,000° C. for the raw ore, depending upon the composition. Zirkite is an excellent refractory within the limits set by its softening and melting points, but the low melting point obviously detracts greatly from the refractory value of the ore. It has been used successfully as raw material in the manufacture of combustion boats, tubes, etc., for high temperature work in the laboratory; but the successful use of the material on a large scale awaits the development of means of raising the melting point.

The problem obviously is the elimination of the element or elements which exert so detrimental an effect upon the melting point of the ore. No definite information is available regarding the specific effect of the various impurities upon the melting point of pure zirconium oxide, but silicon and iron, which together constitute the bulk of the impurities, naturally are regarded as the chief sources of trouble.

Methods of purification, as recorded in the literature, may be divided into two classes:

<sup>2</sup> Meyer: *Foote Mineral Company publication for November, 1916.*

<sup>3</sup> Meyer: *Met. Chem. Eng.*, 1914, XII., 791; *Audley: Trans. Ceram. Soc.*, 1917, XVI., 121; *Rosenhain: Trans. Faraday Soc.*, 1917, XII., 178; *Devereux: Met. Ind.*, 1920, XVI., 414.

(1) Methods for the preparation of pure zirconium compounds.<sup>4</sup>

(2) Methods for partial purification of the ore by elimination of impurities, either by leaching<sup>5</sup> or by volatilization.<sup>6</sup>

Those methods in the first class which are successful are adaptable only for the production in the laboratory of small amounts of pure zirconium compounds. The methods in class two have been confined almost entirely to the removal of iron. The refractory silicates of zirconium were not affected at the relatively low temperatures used in Phillips' chlorination experiments and are not susceptible to leaching unless they have been recomposed by a preliminary fusion.<sup>7</sup> The methods in this class are better adapted for large scale operation but are successful only to a limited extent in producing satisfactory refractory material from the raw ore.

The remarkable stability at high temperatures of certain compounds of zirconium, particularly the oxide and carbide, together with the fact that these compounds are not appreciably volatile below their decomposition points, suggested the use of electric heating as a means of purifying zirkite ore by the elimination of impurities whose oxides and carbides presumably are less refractory than the corresponding zirconium compounds. Hitherto

the electric furnace has been employed<sup>8</sup> only as a preliminary step in the purification of zirkite, apparently for the sole purpose of decomposing refractory silicates. This investigation, therefore, was undertaken for the sake of ascertaining to what extent zirkite might be freed from impurities by direct heating in an electric furnace.

Before the experimental portion of this investigation could be undertaken, a scheme of analysis had to be outlined. A search of the literature revealed many conflicting statements, and considerable time was devoted to the investigation of the various methods before a satisfactory scheme was obtained. A brief, critical review of some of the methods proposed, together with a description of the scheme adopted, is therefore included in this report.

#### THE ANALYSIS OF ZIRCONIUM COMPOUNDS.

The characteristic properties of zirconium ores which make them valuable, *i.e.*, the refractory properties and chemical inertness, formed the first obstacles to be overcome in the decomposition of the ore.

Four general methods of attack have been proposed:

(1) Fusion with hydrofluoric acid or with fluorides.<sup>9</sup>

(2) Conversion to carbides in the electric furnace.<sup>10</sup>

(3) Fusion with sulphuric acid or its derivatives.<sup>11</sup>

<sup>4</sup> Berlin: *Jour. prakt. Chem.*, 1853, LVIII., 147; Hermann: *Ibid.*, 1866, XCVII., 330, 340; Bailey: *Chem. News*, 1886, LIII., 55, 260, 287; Doremus: *Jour. Am. Chem. Soc.*, 1886, VIII., 91; Bayer: *Zeit. angew. Chem.*, 1910, XXIII., 485; Anonymous: *Ceramique*, 1911, XIV., 204; Loveman: *U.S. Patent No.* 1,261,984, 1918; Imray: *British Patent No.* 16,555, 1913; Leuchs: *German Patent No.* 285,344, 1914; Meyer: *loc. cit.*, and Granger: *loc. cit.*

<sup>5</sup> Wedekind: *Zeit. angew. Chem.*, 1908, XXI., 2270; Weiss and Lehmann: *Zeit. anorg. Chem.*, 1909, LXV., 178; Wedekind: *Ber. deutsch. chem. Ges.*, 1910, XLIII., 290; Ramsden: *Met. Ind.*, 1920, XVI., 3; Audley; Granger; Rosen: *loc. cit.*

<sup>6</sup> Phillips: *Jour. Am. Ceramic Soc.*, 1918, I., 791.

<sup>7</sup> Weiss and Lehmann: *loc. cit.*, Jost and Plocker: *German Patent No.* 285,981, 1914.

<sup>8</sup> Moissan: *Comptes rendus*, 1893, CXVI., 1222; Troost: *Ibid.*, 1893, CXVI., 1428; Podszus: *Jour. Soc. Chem. Ind.*, 1917, XXXVI., 217; Barton: *U.S. Patent No.* 1,342,084, 1920; Weiss and Lenmann: *loc. cit.*

<sup>9</sup> Marignac: *Ann. Chim. Phys.*, 1860 (3), LX., 260; Weiss and Neumann: *Zeit. anorg. Chem.*, 1909, LXV., 248; Anonymous: *The Brass World*, 1911, VII., 46; Meyer: *Footnote Mineral Company Publication for November*, 1916; Weiss and Lehmann: *loc. cit.*

<sup>10</sup> Granger: Moissan; Podszus; Troost; Weiss and Lehmann: *loc. cit.*

<sup>11</sup> Baskerville: *Jour. Am. Chem. Soc.*, 1894, XVI., 475; Dittrich and Freund: *Zeit. anorg. Chem.*, 1907, LVI., 337; Weiss: *Ibid.*, 1910, LXVII., 456; Wedekind: *Ber. deutsch. chem. Ges.*, 1910, XLIII., 290; Johnstone: "The Rare Earth Industry," 1915; Powell and Schoeller: *Analyst*, 1919, XLIV., 397; Weiss and Lehmann; Bayer: *loc. cit.*



(4) Fusion with alkalis.<sup>12</sup>

Fusion with sodium tetraborate (borax) was found to furnish the best means for the decomposition of the materials encountered in this investigation. Borax fusions usually produce complete decomposition in one operation, but the boric acid must be eliminated thereafter if a complete analysis is desired. Fusion with alkalis produces decomposition of the silicates and phosphates, but is not applicable to oxide ores. Fusion with pyrosulphates decomposes oxide ores, but is not applicable to silicates. Methods involving fusion with fluorides or conversion to carbides in the electric furnaces are objectionable on account of loss through volatilisation. A combination of alkali fusions, followed or preceded by pyrosulphate fusions, eventually produces complete decomposition and total solution of any zirconium compound, but the procedure is tedious and involved. In all cases the method employed for decomposition is determined by the nature and characteristics of the material.

After the ore has been decomposed by fusion methods and brought into complete solution, the problem of the separation of the various elements arises.

## ANALYTICAL SEPARATIONS.

Silicon is removed from the solution without difficulty owing to the insolubility in acids of its dehydrated oxide.

Iron interferes with almost all of the methods for the precipitation of zirconium from solution, and should be removed before such precipitation is attempted. Leaching of freshly precipitated or ignited oxides by acid solutions, including oxalic and sulphurous acids<sup>13</sup> is not successful.<sup>14</sup> Smith<sup>15</sup> claims to have effected complete separation of iron and zirconium by electrolytic methods, using a mercury cathode,

and Price<sup>16</sup> records the formation of soluble perzirconates by methods which would leave the iron insoluble. Neither of these results could be duplicated during this investigation.

Only two really successful methods have been devised for the separation of iron from solutions containing zirconium. These are based, respectively, upon selective solubility of ferric chloride in ether,<sup>17</sup> and the fact that iron is and zirconium is not precipitated by hydrogen sulphide from ammoniacal solutions containing tartaric acid.<sup>18</sup> The ether separation method is the better of the two for the removal of large amounts of iron such as are encountered in the analysis of zirconium steels or ferro-zirconium. The precipitation method is not as satisfactory for the removal of large amounts of iron, owing to the difficulties encountered in handling large volumes of precipitated ferrous sulphide. It is indispensable, however, for the removal of the traces of iron which almost invariably survive the ether separation, and is adaptable for the analysis of zirconium ores in which the iron oxide content does not greatly exceed five per cent.

A few attempts to precipitate zirconium and titanium separately are recorded in the literature,<sup>19</sup> but the success of some of these attempts has been questioned.<sup>20</sup> For analytical purposes the separation of zirconium from titanium is unnecessary, as titanium is readily determined by Weller's<sup>21</sup> colorimetric method using hydrogen peroxide. The presence of zirconium does not interfere with this determination.

A variety of methods have been proposed for the simultaneous precipitation of zirconium and titanium. Dittrich and

<sup>16</sup> Price: "Per-Acids and Their Salts," 1912.

<sup>17</sup> Noyes, Bray and Spear: *Jour. Am. Chem. Soc.*, 1908, XXX., 481.

<sup>18</sup> Wedekind: *loc. cit.*

<sup>19</sup> Bailey: *Jour. Chem. Soc.*, 1886, XLIX., 149; Crookes: "Select Methods in Chemical Analysis," 1894; Dittrich and Freund: *loc. cit.*; Browning, Simpson and Porter: *Am. Jour. Science*, 1916, XLII., 106; Headden: *Chem. Abstracts*, 1917, XI., 2311.

<sup>20</sup> Matthews: *Jour. Am. Chem. Soc.*, 1898, XX., 815; Weiss and Lehmann: *loc. cit.*

<sup>21</sup> Weller: *Ber. deutsch. chem. Ges.*, 1882, XV., 2599.

<sup>12</sup> Jewett: "Bibliography of Zirconium," 1893; Dennis and Spencer: *Jour. Am. Chem. Soc.*, 1896, XVIII., 674; Abegg: *Handbuch*, 1913, IV., 490; Schiötz: *Chem. Abstracts*, 1918, XII., 661; Travers: *Chim. Ind.*, 1919, II., 385; Lundell and Knowles: *Jour. Am. Chem. Soc.*, 1920, XLII., 1439; Bayer; Berlin; Johnstone; Powell and Schoeller: *loc. cit.*

<sup>13</sup> Dubois and Silveira: *Ann. Chim. Phys.*, 1820 (1) XIV., 110; Berthier: *Ibid.*, 1832, (2) L., 362; Wunder and Jeanneret: *Zeit. analyt. Chem.*, 1911, L., 733.

<sup>14</sup> Berlin; Hermann: *loc. cit.*

<sup>15</sup> Smith: "Electro-Analysis," 1911.

Freund<sup>22</sup> claim that sodium acetate will produce complete precipitation of zirconium and titanium. The use of sulphurous acid or its derivatives has been proposed,<sup>23</sup> but Johnstone<sup>24</sup> says that this reagent also precipitates some of the rare earths as well as traces of iron and aluminum, and Hermann<sup>25</sup> reports that the separation resulting from the use of sulphur dioxide is not satisfactory. A number of these separations were attempted during the present investigation with complete lack of success. The manipulation is tedious, precipitation seldom is complete, and the precipitate usually is badly contaminated. Precipitation of zirconium and titanium by weak organic bases has been recommended,<sup>26</sup> and a number of these precipitations were attempted, using phenylhydrazine as the most promising member of this class. The experiments uniformly were unsuccessful, the precipitation was slow and incomplete, and the precipitate usually was contaminated. Variations of Hillebrand's method for the precipitation of zirconium phosphate<sup>27</sup> have been recommended. Lundell and Knowles<sup>28</sup> discuss the method in detail, and point out that the variations in composition of the precipitate prevent the use of the method except for very small amounts of zirconium.

<sup>22</sup> Ditrlich and Freund: *loc. cit.*

<sup>23</sup> Berthier: *Ann. Chim. Phys.*, 1832, (2) L., 362; 1843, (3) VII., 84; *Chancel: Jour. prakt. Chem.*, 1858, LXXIV., 471; *Imray: Jour. Soc. Chem. Ind.*, 1890, IX., 941; *Trautmann: Zeit. angew. Chem.*, 1911, XXIV., 62; *Baskerville; Ditrlich and Freund; Weiss and Lehmann; Travers; Granger; Powell and Schoeller: loc. cit.*

<sup>24</sup> Johnstone: *loc. cit.*

<sup>25</sup> Hermann: *Ibid.*

<sup>26</sup> Hess and Campbell: *Jour. Am. Chem. Soc.*, 1899, XXI., 776; *Jefferson: Ibid.*, 1902, XXIV., 540; *Allen: Ibid.*, 1903, XXV., 421; *Hartwell: Ibid.*, 1903, XXV., 1128.

<sup>27</sup> Hillebrand: *U.S. Geol. Survey, Bull. No. CXLVIII.*; *Biltz and Mecklenburg: Zeit. angew. Chem.*, 1912, XXV., 2110; *Ferguson: Eng. Min. Jour.*, 1918, CVI., 356, 793; *Steiger: Jour. Wash. Acad. Sci.*, 1918, VIII., 637; *Nicolardot and Reglade: Comptes rendus*, 1919, CLXVIII., 348; *Browning, Simpson and Porter: loc. cit.*; *Schlotz: loc. cit.*

<sup>28</sup> Lundell and Knowles: *Jour. Am. Chem. Soc.*, 1919, XLI., 1801.

The most satisfactory method for the analytical determination of zirconium and titanium was found to be precipitation by cupferron, the ammonium salt of nitrosophenylhydroxylamine. The use of this reagent has been proposed by several authors,<sup>29</sup> and has been recommended recently by Lundell and Knowles,<sup>30</sup> who discuss the method in detail, including a list of the elements which interfere with the precipitation and a discussion of the precautions which must be observed.

The filtrate from the cupferron precipitation contains the aluminum, rare earths, and traces of other elements. The scheme of separation for the elements in this filtrate depends upon the nature and number of elements present, as determined in the preliminary qualitative examination.

From the foregoing data a complete scheme of analysis, adaptable to low-phosphorus baddeleyite ore, was evolved. In view of the time and labour required for a complete analysis, a modified scheme was adopted for the numerous analyses which attended the progress of this investigation. This modified scheme allows only the determination of silicon, iron, titanium, and zirconium, as follows:

#### MODIFIED SCHEME FOR ROUTINE ANALYSIS.

The sample is ground to 80-100 mesh. 0.5 gram of the sample is weighed out and fused<sup>31</sup> in platinum with 5 grams of borax until a clear, fused mass results. When fusion is complete (usually requiring about one-half hour at the full heat of a Meker burner) the crucible is removed from the flame. While solidification of the melt is taking place, the crucible is kept in motion so that when cold the fusion is distributed around the sides of the crucible. The cooled melt is dissolved in 5 per cent. hydrochloric acid in a porcelain casserole, solution being hastened by gentle warming. When solution is complete, the crucible is removed and rinsed out, 10-15 cc. concen-

<sup>29</sup> Ferrari: *Chem. Abstracts*, 1915, IX., 1019; *Thornton and Hayden: Am. Jour. Sci.*, 1914, XXXVIII., 137; *Thornton: Ibid.*, 1916, XLII., 151; *Brown: Jour. Am. Chem. Soc.*, 1917, XXXIX., 2358.

<sup>30</sup> Lundell and Knowles: *Jour. Ind. Eng. Chem.*, 1920, XII., 344.

<sup>31</sup> The usual practice is to dehydrate the borax in the crucible, add the weighed sample, and proceed with the fusion. Carbide samples should be ignited to the oxides before attempting the fusion.

trated sulphuric acid are added, and the solution is evaporated on a hot plate until fumes of sulphur trioxide appear. The final fuming is done over a free flame, agitating the solution to prevent spattering. The residue is cooled, dissolved by diluting with water, and filtered. The precipitate on the filter is washed with hot water, ignited, weighed, treated with hydrofluoric and sulphuric acids, again ignited and weighed, and the loss of silica determined. A slight residue, mainly iron, is recovered by fusion with pyrosulphate and added to the original filtrate.

The filtrate from the removal of silica is diluted to about 500 cc., precipitated with ammonia, and boiled to coagulate the precipitate. After settling, the supernatant liquid is decanted as completely as possible to remove the bulk of the alkalis and boron. The ammonia precipitate is redissolved by adding 5-10 cc. of concentrated sulphuric acid. One gram of tartaric acid is added, and the solution is made distinctly ammoniacal. The volume of the solution at this point should be 150-200 cc. The solution is treated with hydrogen sulphide for twenty minutes, boiled for 3-4 minutes, allowed to cool, and filtered. The precipitate is covered and allowed to drain thoroughly, but is not washed, owing to the decided tendency of the ferrous sulphide to pass through the filter when any washing solution is used. The filtrate is subjected to a second precipitation with hydrogen sulphide, and is again boiled and filtered. The two precipitates of ferrous sulphide are redissolved in dilute *aqua regia* and the iron is determined gravimetrically. The presence of hydrochloric acid and small amounts of organic matter (from the tartaric acid) precludes the determination of iron by volumetric methods.

The filtrate from the removal of ferrous sulphide, boiled to remove most of the hydrogen sulphide, is made acid with a known excess of sulphuric acid, boiled again, and the precipitated sulphur filtered off and discarded. The filtrate is cooled, diluted to 600 cc. containing 7.5-10 per cent. free sulphuric acid, chilled in ice water, and precipitated by the addition of a cold 6 per cent. aqueous solution of cupferron. During this precipitation the temperature must not exceed 15° C. The precipitate is allowed to stand one-half hour, and is then filtered, using gentle suction and washing with cold 5 per cent. hydrochloric acid. The filtrate and washings are discarded. The precipitate is ignited and

weighed as  $ZrO_2 + TiO_2$ .<sup>32</sup> The weighed precipitate is fused with pyrosulphate, dissolved in 5 per cent. sulphuric acid, and the titanium determined colorimetrically.

On account of the variable amounts of carbon in the different samples, the analytical results were computed to a metallic basis, and the ratio of the elements determined on the basis of 100 parts of metallic zirconium. For the comparison of the various electric furnace products a study of this ratio is more easily understood than a study of the percentage composition of the samples.

#### EXPERIMENTAL.

The zirconium ore employed in this investigation was a finely ground zirkite, 65 per cent. of which passed through a 100-mesh sieve. Duplicate analyses of ignited samples of the ore gave the following composition:

	Per cent.	Per cent.
ZrO <sub>2</sub> .....	72.55	72.78
SiO <sub>2</sub> .....	17.34	17.26
Fe <sub>2</sub> O <sub>3</sub> .....	4.11	4.14
TiO <sub>2</sub> .....	0.80	0.81
Al <sub>2</sub> O <sub>3</sub> .....	5.28	5.91
Rare Earths (cerium group) .....	1.04	1.13
P <sub>2</sub> O <sub>5</sub> .....	0.49	0.45
MnO <sub>2</sub> .....	0.25	0.27
MgO .....	trace	trace
Total .....	101.86	102.75 <sup>33</sup>
Loss on ignition ...	2.88	2.88

Ratio, on a metallic basis, of the elements present in the ore:

100 Zr : 15.1 Si : 5.37 Fe : 0.89 Ti

<sup>32</sup> Any iron which escapes the precipitation with hydrogen sulphide will appear in this precipitate. Experience has shown, however, that the amount of iron which survives a double precipitation with hydrogen sulphide is so small that it may be disregarded for all except the most exact determinations. The colour of this ignited precipitate is a reliable indicator of the composition. A pure white colour indicates that zirconium alone is present. Titanium produces a yellow colour, and a reddish or brownish tinge indicates the presence of iron.

<sup>33</sup> The error in the analyses probably is due to adsorption of alkalis by the cupferron precipitate; but may be due in part to the existence in the ore of elements, e.g., iron and manganese, in different states of oxidation than the ones represented in the above table. The composition of the silicates of zirconium, which occur in zirkite ore, has not been determined definitely.

Owing to the time and labour consumed by the necessary analytical work, it was decided to limit this investigation to the three impurities, silicon, iron and titanium. Since silicon is present in far larger amounts than any other impurity, this investigation was directed primarily towards the elimination of silicon. The removal of iron is a secondary object of the investigation.

Two possibilities were considered for the removal of silicon and iron in the electric furnace:

(1) Reduction of the oxides to the metals in the presence of an excess of iron, forming ferro-silicon which could be removed subsequently by mechanical means.

(2) Reduction of the oxides to the metals or carbides with subsequent volatilisation resulting from the application of higher temperatures.

The first method was tried out in a small crucible furnace heated by a direct arc. Iron oxide was added to the charge in an amount sufficient to unite with all of the silicon to form ferro-silicon containing 50 per cent. iron. Several runs were made, but no evidence of the formation of ferro-silicon was obtained. In every case the iron and silicon remained distributed uniformly throughout the charge, probably on account of the high viscosity of the melt which prevented the desired formation and coalescence of ferro-silicon. Increasing the temperature would increase the fluidity of the melt, and a point might be reached at which the ferro-silicon would coalesce and settle out. The indications are, however, that the desired degree of fluidity would not be reached below the temperature at which silicon becomes volatile. If it is necessary to employ temperatures high enough to cause at least partial volatilisation of the impurities, it would seem advisable to rely wholly upon volatilisation to remove the impurities. The latter method also would avoid contaminating the ore by the addition of iron, which is necessary if the ferrosilicon scheme is followed. Accordingly, the attempts to eliminate silicon and iron, as ferro-silicon, were abandoned in favour of attempts to volatilise the impurities directly.

Preliminary experiments conducted in a small arc furnace indicated that zirconium carbide is stable at temperatures above the decomposition point of silicon carbide (car-

borundum).<sup>34</sup> This led to the belief that conversion of the entire ore to carbides, followed by the exposure of the mixed carbides to temperatures above 2,220° C., at which temperature silicon carbide decomposes, would eliminate silicon and perhaps some or all of the iron and other impurities. If this elimination of impurities were successful, it would then be possible to initiate the zirconium carbide to the oxide, thus producing pure and highly refractory zirconia.

The first experiments were carried out in a furnace of the silicon carbide type, sufficient carbon being added to ensure the transformation of all the oxides present into carbides. Later experiments were performed in an arc furnace, the amount of carbon being varied from run to run.

#### EXPERIMENTS WITH A RESISTANCE FURNACE.

The resistance furnace was built in the form of a rectangular trough 7 inches wide at the bottom, 8 inches wide at the top, 9 inches deep, and 29 inches long. The floor was built of zirkite brick supported by a double layer of fire brick. The sides were built of fist-size lumps of zirkite, backed with the fire brick and faced smooth with ground zirkite bonded with a little water-glass. The sides and floor were permanent. The end walls were faced with zirkite brick, which were backed up with fire brick, and were torn out after each run to facilitate removal of the charge. The electrodes were pieces of 4-inch square carbon electrodes, which entered through the centre of the end walls and protruded four inches into the furnace. The outer ends of the electrodes were water-cooled and connected to bus bars by flexible leads. Power was supplied by a 75 kilowatt motor-generator set. Two thousand amperes was the largest current available, representing the maximum output of the motor-generator set.

The complete conversion of 100 parts of ore to the various carbides and carbon monoxide requires approximately 33 parts of carbon. To ensure the presence of an excess of carbon, a ratio of 45 parts of carbon to 100 parts of ore was used. Petroleum coke, 10-20 mesh in fineness, supplied the carbon for most of the runs, although in one or two cases granular electrode carbon was tried.

Four runs were made in the resistance

<sup>34</sup> Gillett: *Jour. Phys. Chem.*, 1911, XV., 213.

furnace. Since the runs were all more or less alike, the first one only will be described in detail, as follows:

RUN 1.

Ratio of ore to carbon in charge .....	100 : 45
Total weight of charge ...	86.5 pounds
Core .....	A double line of graphite electrode pieces, one inch in diameter, the junctions packed in petroleum coke to ensure contact
Duration of run .....	1 hour, 52 min.
Power consumption .....	60 K.W.H.

The charge was packed loosely in the furnace up to the level of the electrodes. The core was inserted and the remaining charge added, filling the furnace. At first it required a potential of 46 volts to produce a current of 400 amperes through the furnace. Small gas volcanoes appeared almost at once, followed by flames, bright yellow at the base, with reddish yellow tips. The power input was maintained as high as possible, being limited by the violence of the gas evolution which resulted in loss of charge when the power input became too high. After the first violent evolution of gas subsided, the charge presented the appearance of gentle boiling. After half an hour, when the total power input had reached 15 K.W.H., one end of the charge ceased boiling and settled to form a crust. This effect spread gradually until the entire charge was crusted over and quiet. Heating was continued about half an hour more. The entire charge

finally became bright red in colour, but the temperature could not be raised further. At first the current was carried almost entirely by the core; but the charge itself soon began to conduct with the result that the current rose and the voltage fell off rapidly, until at the end of the run the current reached 1,750 amperes and the voltage dropped to 5. These results made it evident that the conductivity of the core and heated charge was too great to allow the input of power at a rate sufficient to produce the very high temperature desired.

When the cooled charge was examined, a greyish black granular core about 4 inches in diameter was found in the centre, extending the length of the charge between the electrodes. Small deposits of spongy material, metallic in appearance and rather bluish in colour, which subsequent examination proved to be zirconium carbide, were found in close proximity to the original core. The total weight of "sponge" was about six pounds. The remaining contents of the furnace consisted of unchanged charge. The original graphite core was not attacked, indicating the presence of an adequate supply of carbon in the charge. Some slight indications of the volatilisation of silica were found on the furnace walls, but the power input evidently was too low.

The three subsequent runs were made in an attempt to increase the power input, but without marked success. The results of the four runs may be summarised as follows:

TABLE I.

K.W.H.	Av. Kw.	Carbide "sponge" pounds	Metal in Sponge when Zr = 100		
			Si	Fe	Ti
60	32	6.0	3.7	4.48	0.79
75	34	6.5	11.0	5.50	0.78
100	38	10.0	12.2	7.60	0.79
80	40	7.5	5.5	2.60	0.87
		Original Ore	15.1	5.37	0.89

The behaviour of the carbide "sponge" on analysis showed that most of the silicon was present as the carbide, thus indicating that in general the temperature of the mass was not high enough to ensure the removal of the silicon by volatilisation. As the data indicate, the removal of silicon varied in a very irregular manner, being fairly complete in some cases but very incomplete in others. Other samples from portions of the charge farther removed from

the core showed higher ratios of silicon to zirconium. This follows naturally, since volatilisation of silicon would occur first in the hottest portion of the charge, *i.e.*, around the core, and would be less evident in regions at a greater distance from the source of heat.

The data indicate little or no elimination of titanium or of iron, except in the fourth run, where considerable iron was apparently removed. In this run, however,

about 9 pounds of common salt was added to the charge resulting in the elimination of approximately half the iron, presumably through the formation of the volatile chloride. All things considered, the results obtained with the resistance furnace were unsatisfactory, and this type of furnace was abandoned in favour of one of the arc type.

#### EXPERIMENTS WITH AN ARC FURNACE.

The furnace shell of the arc furnace consisted of an iron pot, lined with fist-sized pieces of zirkite ore. The lining was faced smooth with ground zirkite bonded with a little water glass, and contained the same ratio of carbon to zirkite as the charge proper. The resulting hearth was cone-shaped, 8 inches in diameter at the top, 4 inches in diameter at the bottom, and 8-10 inches deep. This lining was torn out after each run to facilitate removal of the charge. The lower, horizontal electrode, composed of two 2-inch square graphite electrodes, formed the floor of the hearth, entering through a rectangular opening in the side of the cast iron pot. The upper electrode was a 4-inch square carbon electrode, suspended in a vertical position and counter-weighted to allow adjustment. Both electrodes were clamped in water-cooled electrode holders and connected to bus bars by means of flexible cables.

The first run performed in this furnace will be described in detail, as being typical of all the runs carried out subsequently.

#### RUN 5.

Ratio of ore to carbon in charge ..... 100 : 45  
 Total weight of charge ..... 11 pounds  
 Time of run ..... 45 minutes  
 Power consumption ..... 32.5 K.W.H.

The run was started by striking an arc between the bare electrodes. The walls of the cone immediately began to slag down so that the first addition of charge was made as soon as possible after starting the arc. The charge was fed in slowly and was observed to solidify when it reached the zone of the arc. During the early stages of the run the arc was smothered by the charge, but after all the charge had been added the arc was run open, and remained fairly quiet. The current was maintained at about 1,000 amperes until the evolution of fumes had almost ceased, when the arc became noisy and hard to maintain. The run was stopped when this point was reached.

The top of the charge oxidised during cooling, forming a layer of fine white oxides, below which lay a brittle, black mass weighing approximately 3.5 pounds. A sample for analysis was taken from the centre of this cake, and gave the following ratio:

100 Zr : 4.85 Si : 6.38 Fe : 0.70 Ti

A series of runs was made in which the ratio of carbon (petroleum coke) to zirkite ore was varied systematically. The results are assembled in the following tables.

TABLE II.

Effect of Varying Ratio of Ore to Carbon.

Run	Charge Pounds	Carbon per 100 ore	K.W.H.	Yield purified product pounds
5	11.0	45	32.5	3.5
9	12.5	25	18.25	3.0
10	12.0	20	17.5	3.1
11	15.4	15	21.5	5.0
18	15.4	10	19.3	7.0
19	16.8	5	27.0	9.9

TABLE III.

Elimination of Impurities.

Metal Ratio in Product.					Percentage elimination of				
Run	Zr	Si	Fe	Ti	Run	Carbon per 100 ore	Si	Fe	Ti
5	100	4.85	6.38	0.70	5	45	68	-19	21
9	100	3.03	6.50	0.64	9	25	80	-21	28
10	100	2.21	5.00	0.55	10	20	85	7	38
11	100	0.88	5.92	0.70	11	15	94	-10	21
18	100	1.31	8.73	0.69	18	10	91	-62	22
19	100	1.86	6.67	0.73	19	5	88	-24	18
Ore	100	15.70	5.37	0.89					

The data obtained with the arc furnace show a maximum in the removal of silicon when the ratio of zirkite to carbon is 100 : 15. Calculations based on the silica content of the ore show that a little more than 10 parts of carbon to 100 parts of ore is just enough to transform all of the silica into carbide (carborundum) and carbon monoxide. We have, therefore, come to conclusion that the best high-temperature elimination of silicon is obtained when little more than enough carbon is used to form carbide with the silicon only, leaving the zirconium oxide undecomposed.

When more than 15 parts of carbon are used the elimination of silicon becomes steadily less complete. Under these circumstances it is known that zirconium carbide is actually produced in the arc. The zirconium carbide therefore appears to retain some of the silicon and the suggestion is offered that stable double carbides of silicon and zirconium may be produced or that the two carbides form solid solutions or mixed crystals. Runs in which granular electrode carbon was substituted for petroleum coke showed that better results may be obtained on a small scale with the more finely divided coke.

An interesting fact brought out by these experiments is the high melting point and stability, in a reducing atmosphere, of the carbide of zirconium. As long as there was an excess of carbon present, over and above the amount required for the complete conversion of the oxides to carbides, it was impossible to melt the product even under the direct action of a 40-50 kilowatt arc.

*(To be Continued.)*

#### BACTERICIDAL PROPERTIES OF THE PRODUCTS OF RADIUM EMANATION.

By JOHN ALBERT MARSHALL, COLLEGE OF DENTISTRY, UNIVERSITY OF CALIFORNIA.

*Communicated, October 7, 1922.\**

The following abstract deals with a description of the use of radium therapy in periapical infections,<sup>1</sup> and supplements a preliminary note<sup>2</sup> in which it was pointed out that solutions of the products of radium emanation possess distinct bactericidal properties. Additional data have been compiled, but the analysis of them clearly indicates that with the present-day knowledge it is impossible to state definitely and conclusively why the products of the emana-

tion produce such characteristic effects.

Although it was reported in 1909<sup>3</sup> that radium exerts an inhibitory influence on pathogenic and non-pathogenic organisms, no further work was done in this field until ten years later, when the former observations were confirmed.<sup>4</sup> Bacteria of various types were exposed to radium emanation with the result that a distinct inhibitory effect upon the cultures was observed.

In this present experiment a solution of the products of radium emanation is employed. The emanation tubes are usually discarded by the laboratories after they have undergone disintegration in respect to their content of gamma ray. However, they still contain in varying proportions radium A, B, C, and D. The effects which have been obtained are presumably not due to the hard gamma ray, but result in all probability from the action of the softer beta ray.

The radioactive solution is prepared as follows: a "de-emanated" emanation tube is placed in a sterilised mortar of about 20 cc. capacity, covered with Ringer's solution and then crushed with a pestle. On account of the rapidity with which the radioactivity of this solution diminishes, it is advisable to crush the tubes immediately before use. This solution is carried directly to the infected area by means of sterile dressings. In the case of chronic or acute apical abscesses, found about the roots of teeth, the radioactive liquid is forced into the infected area through the pulp canal of the tooth and allowed to remain for 24 hours. Subsequently the dressings are removed, the canals tested for sterility and finally filled. With two possible exceptions there has been no evidence, after three years of time, of succeeding soreness or pain. The individual dosage in terms of millicuries of gamma radiation has varied from 0.046 to 0.138.

Failures in this method of treatment have been recorded, but the fact remains that sterile tests have been obtained more often by using the radioactive solution than in similar experiments with other antiseptic agents.

Summaries of experimental and clinical data are presented which indicate the variations in the pathology, age of patient, etiology, treatment, clinical result and laboratory findings.

In many instances tubes have been used in which de-emanation had proceeded to such a degree that it was not possible to obtain a reading by the electroscope. These

have given similar results insofar as bactericidal action is concerned, but they have not caused the soreness which sometimes accompanies the use of solutions containing a recorded amount of gamma rays.

In general the cases selected have been those in which previous treatments were without satisfactory result. Dichloramin T, formocresol beechwood cresote, phenol, and other antiseptics of a similar nature had been used without producing a noticeable change in condition. In fact, the greater majority of the cases carried a history of unsuccessful treatment. Most of them yielded to the action of the radioactive solution.

The precautionary measures which are to be observed are naturally those referring to dosage and technique of application. Severe radium burns resulted in monkeys when emanation tubes containing eighteen milluries were sealed into pulp canals of central incisors. These burns were so extreme that the hard palate and orbit were involved. It is believed to be impracticable to use the radium except as a solution of the solids. The tubes should be thoroughly crushed under Ringer's solution exactly at the moment of use, and it has been customary to have three or four patients prepared and ready at one time in order to secure the greatest economy of material. The limited availability of de-emanated tubes except at emanation laboratories is a serious drawback to an extensive application of this therapy. However, it is planned, if funds become available, to further extend these researches to include not only additional data upon dosage, but also to report upon the application of other radioactive preparations which may be found to be more plentifully distributed.

\* *Proceedings of the National Academy of Sciences of the United States of America*, November 15, 1922.

<sup>1</sup> Marshall, John A., "Radium in Periapical Infections" (in press).

<sup>2</sup> Marshall, John A., "Bactericidal Action of Solutions of Radium Emanation," *Calif. State Med. J.*, Jan., 1922.

<sup>3</sup> Iridell and Minett, "Notes of the Effect of Radium in Relation to Some Pathogenic and Non-Pathogenic Organisms," *Lancet*, 1909, I., p. 1445.

<sup>4</sup> Lequeux and Chrome, "Action of Radium on Bacteria," *Arch. Memo. Obst. gynec.*, Dec., 1919, III., p. 698.



This list is specially compiled for the *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

*Latest Patent Applications.*

34397—Chemical and Metallurgical Corporation, Ltd.—Continuous process for conversion of lead chloride into sulphate, and recovery of hydrochloric acid. Dec. 16.

*Abstract Published this Week.*

**Chromium Compounds.**—Patent No. 187636.—A Patent has been granted to Messrs. C. K. Potter, of 1, St. George's Square, St. Amnes-on-Sea, and F. Robinson, of 225, Green Lane, Bolton, both in Lancashire, for a process for the preparation of chromium compounds, such as chromium oxide, chromium sulphate, acetate, carbonate, and chloride, chrome alum, sodium and potassium chromates, iron sulphate.

Chromite is decomposed by treatment with sulphuric acid and an oxidizing agent, such as chromic acid, at a temperature above 150° C., the oxidizing agent, whether added directly to the reaction-mixture or generated *in situ* by electrolysis, being present in amount insufficient to oxidize the iron completely. The chromite may first be treated with carbonaceous matter or a gaseous reducing agent at a red heat and part of the iron then extracted with dilute acid. Under the conditions set out above, the chromium and part of the iron are converted into insoluble sulphates, from which the chromium is separated by adding a reducing agent to the diluted reaction-mixture when the ferric sulphate is reduced, leaving a residue of insoluble chromium sulphate. This compound may be decomposed by boiling in aqueous suspension with caustic alkalis or alkaline-earths, alkali sulphides or carbonates, alkaline-earth carbonates or ammonia to yield chromium hydroxide and/or basic carbonate; it may be heated with caustic soda or potash in presence of air and with the optional addition of other oxidizing agents to yield sodium or potassium chromate; or it may be boiled with strong barium-chloride or -acetate solution to yield the corresponding chromium salt and barium sulphate. Alternatively it may be dissolved in dilute sulphuric acid in presence of ferric oxide, and a small amount of oxidizing agent, and the solution, after reduction of any ferric salt formed, treated with potassium sulphate for the production of chrome alum. Instead of first separating the insoluble chromium sulphate, the mixture of insoluble chromium and iron sulphates obtained in the initial decomposition may be treated directly for the production of chromium oxide. In one process the mixed sulphates are washed and heated with excess of coal in a reducing atmosphere, a mixture of iron sulphide and chromium oxide being obtained. In another process, the mixed sulphates are boiled with a slight excess of alkali-sulphide solution, and the black precipitate obtained ignited in a reducing atmosphere at red heat. In a third process the mixed sulphates are calcined, and the resulting oxides mixed with coal and heated in a reducing atmosphere. In each case the product is treated with acids to dissolve the iron, and the residual chromium oxide may be dissolved in sulphuric acid in presence of a small amount of oxidizing agent and used for the preparation of other chromium compounds.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the official price of 1s. each.



# THE CHEMICAL NEWS,

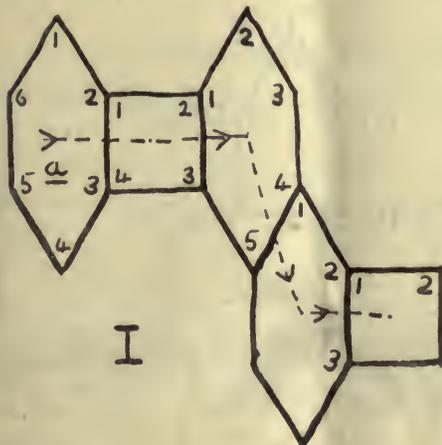
VOL. CXXVI. No. 3275.

## A NEW SYSTEM FOR THE LINEAR REPRESENTATION OF THE STRUCTURE OF ALL ORGANIC COMPOUNDS.

By T. SHERLOCK WHEELER, B.Sc.,  
A.R.C.Sc.I., A.I.C.

The system given below was primarily designed to enable the structure of *all* ring compounds to be represented linearly by a simple arrangement of letters and figures, from which, with the aid of a few rules, the graphical formula could be easily deduced. This is at present possible with the less complicated aliphatic compounds, *e.g.*, adipic acid can be written (COOH). CH<sub>2</sub>.CH<sub>2</sub>.CH<sub>2</sub>.CH<sub>2</sub>.(COOH); the ordinary line of type need not be disturbed to show its structure. But it is far otherwise with ring compounds, and it was a linear system for these compounds which might save the great amount of space that is now perforce devoted in chemical journals, and dictionaries, to printing their extended graphical formula, that the author first sought. In that search he was successful; as the system developed, however, it appeared it could be used equally well to represent all organic compounds, and from the representations thus obtained for any type of compound, names clearly showing the constitution could be deduced.

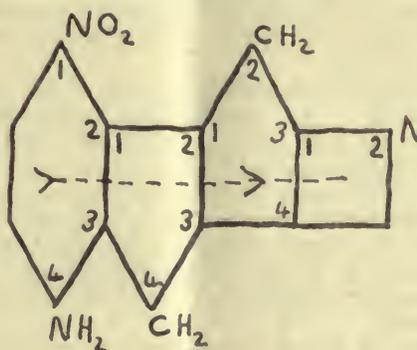
The principle of the system is best outlined by beginning with ring-compounds. I is the graphic formula of a possible aro-



I

matic hydrocarbon. To represent it, the centres of the rings are joined as shown, and one supposes oneself to pass along the dotted line from "a." All rings are numbered independently and clockwise, the first ring is numbered from any carbon, in others the numbering begins on the left hand of one entering the ring along the "structure line." Then I. is Ar. VI. 2, 3 IV. 2, 3 VI. 4, 5 VI. 2, 3 IV. Ar. shows the system to be aromatic, the Roman numerals give the number of elements in each ring, and the carbons common to any ring and the next are shown, left hand carbon first, after the former's Roman numeral, by their numbers in the former. Since the "structure line" always crosses the join of the common carbons, the compound may be said to be represented by describing the course, as it were, of its structure line.

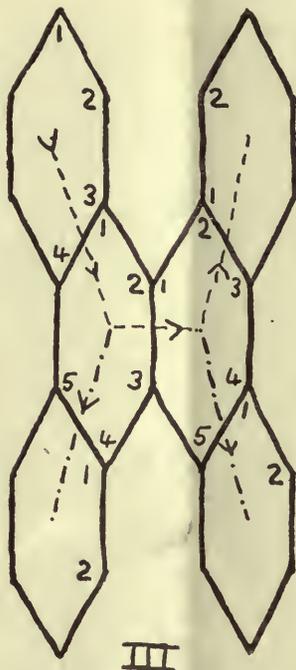
All information about any ring is given in brackets immediately after the numeral representing it. Substituents are indicated by the number of the substituted carbon followed by the chemical symbol of the substituent; should any of the carbons be replaced by another element, the symbol of that element comes *before* the number of



II

its position. In some aromatic compounds it may be necessary in the case of five and other odd-membered rings to show which of the carbons is saturated, *i.e.*, lack the centric bond. This is done by indicating that this particular carbon has two hydrogen atoms attached to it. II. is Ar. VI. (1-NO<sub>2</sub>, 4-NH<sub>2</sub>) 2, 3 V. (4=H<sub>2</sub>) 2, 3 V. (2=H<sub>2</sub>) 3, 4 IV. (N-2).

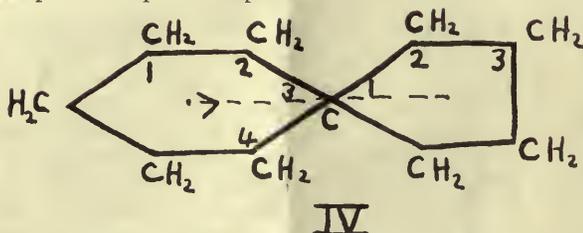
When branches occur in the structure line, the main structure line is given first, and then, separated by semi-colons, the various branches (shown — · — · — ·), the rings from which these latter start being



identified by indices. III. is Ar. VI. 3, 4 VI.' 2, 3 VI." 2, 3 VI.; 4', 5' VI.; 4", 5" VI. In the main structure line it is unnecessary to attach indices to those numbers which refer in the ordinary way to the indexed rings.

Alicyclic compounds are prefixed by the symbol Al. In representing compounds containing both types of rings one symbol holds until cancelled by the other. Double bonds are shown in the usual way—a  $\Delta$  followed by the number of the carbon from which the bond begins. Doubly linked substituents are joined by two hyphens to the number of the carbon to which they are attached.

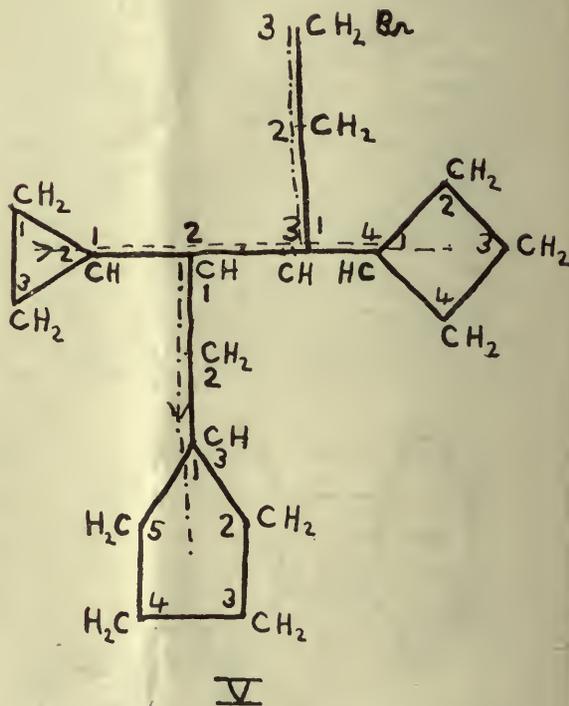
Other than ortho-fused ring systems must now be considered. IV. is a simple example of a spiro compound. It is Al. VI. 3



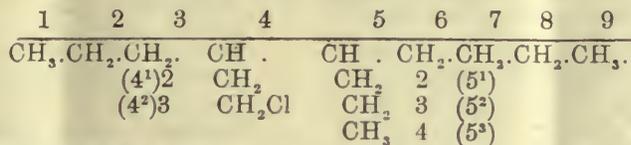
V. The structure line is drawn through the spiro carbon and the numbering of the second ring is clockwise from that carbon. When rings are linked by chains, the

structure line passes along the chain. The chain is indicated by the number of elements in it, but the Roman numeral for a chain has a bar placed over it. The chain is numbered from where the structure line enters it, and in the direction in which that line passes along it. The carbon at which the line leaves the chain is indicated as with rings: the ring to which the chain leads is numbered clockwise from where it is entered. Substituents and non-carbon elements are shown as above; the carbons common to chain and ring are numbered twice as before. The effect of the symbols Ar. and Al. is taken to persist on the far side of a chain. Branches in the chain, which do not lead to rings are numbered and shown on the same plan; the structure line system is used for them as for those that are attached to rings. V. is Al. III. 2  $\overline{\text{IV}}$ . 4  $\overline{\text{IV}}$ .; 2'  $\overline{\text{III}}$ . 3 V.; 3'  $\overline{\text{III}}$ . (3-Br.)

The system can now be applied to any open chain compound. VI. is  $\overline{\text{IX}}$ . 5  $\overline{\text{IV}}$ .; 4'  $\overline{\text{III}}$ . (3-Cl.) The main structure line passes along the principle chain, then along



the longest branch, and so on, being always drawn to be as long as possible. Other branches are given in

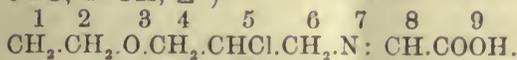


Main Structure line \_\_\_\_\_  
 Branch - - - - -

VI.

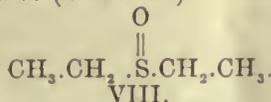
the order of their importance. Neglect of this rule, however, does not cause ambiguity. The Genevan system of "index numbering" for branches could be applied here. Its numbering of the chains is shown in brackets in VI. Using it, VI. would be IX. (4-Et, 5-Pr, 4<sup>2</sup>-Cl). But it is not applicable to ring compounds, and so for the sake of uniformity the structure line system is best applied right through. Also the Genevan system leads to confusion with complicated aliphatic compounds. (See Richter, B., XXIX. (1896), 586).

The following further examples will make the new system clear for aliphatic compounds. VII. is IX. (O-3, N-7, 5-Cl 9=O, 9-OH, Δ')



VII.

VIII. is V. (S-3, 3=O)

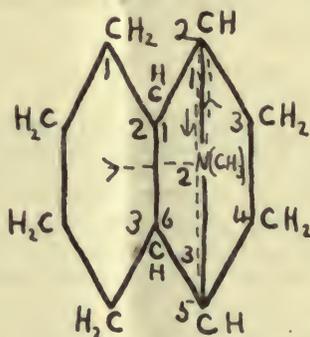


VIII.

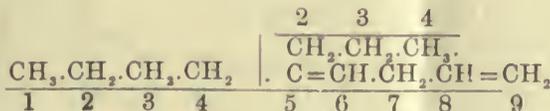
IX. is IX. (Δ<sup>5</sup>, Δ<sup>5</sup>) 5 (IV.)

IX.

It is to be noted that the carbon at which a double bond terminates need never be shown, owing to the exact indication of the chain or ring to which it belongs.



X



(To be Continued.)

PROCEEDINGS AND NOTICES OF SOCIETIES.

ROYAL SOCIETY OF ARTS.

Monday, February 5, 8 p.m. (Canton Lecture): HENRY P. STEVENS, M.A., PH.D., F.I.C., *The Vulcanisation of Rubber.* (Lecture 1.)

Tuesday, February 6, 4.30 p.m. (Dominions and Colonies and Indian Sections): SIR RICHARD A. S. REDMAYNE, K.C.B., M.Sc., M.INST.C.E., M.I.M.E., F.G.S., *The Base Metal Resources of the British Empire.*

Wednesday, February 7, 8 p.m. (Ordinary Meeting): CHARLES R. DARLING, F.Inst.P., A.R.C.Sc.I., *Electrical Resistance Furnaces and their Uses.*

Monday, February 12, 8 p.m. (Canton Lecture): HENRY P. STEVENS, M.A., PH.D., F.I.C., *The Vulcanisation of Rubber.* (Lecture 2.)

Wednesday, February 14, 8 p.m. (Ordinary Meeting): W. J. REES, Lecturer on Refractories in the University of Sheffield, *Progress in the Manufacture of Refractories.*

Friday, February 16, 4.30 p.m. (Indian Section): J. T. MARTEN, I.C.S., M.A.

Imperial Census Commissioner in India, *The Indian Census*, 1921. Sir Edward A. Gait, K.C.S.I., C.I.E., Member of the India Council, will preside.

Monday, February 19, 8 p.m. (Canton Lecture): HENRY P. STEVENS, M.A., Ph.D., F.I.C., *The Vulcanisation of Rubber*. (Lecture 3.)

Wednesday, February 21, 8 p.m. (Ordinary Meeting): C. AINSWORTH MITCHELL, M.A., F.I.C., *Handwriting and its Value as Evidence*. Sir Richard D. Muir will preside.

Wednesday, February 28, 8 p.m. (Ordinary Meeting): PROFESSOR W. E. S. TURNER, D.Sc., Head of Department of Glass Technology, The University, Sheffield, *Heat Resisting Glasses*.

#### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

##### ANNUAL GENERAL MEETING.

The Annual General Meeting of the Society will be held on Wednesday, Feb. 7, at the Chemical Society's Rooms, Burlington House, Piccadilly, W., at 8 p.m.

The accounts for the year will be presented, the President will deliver his annual address, and the election of officers and council for the ensuing term will take place. The appointment of auditor will also take place.

The ordinary monthly meeting of the Society will be held immediately following the Annual General Meeting, when the following papers will be read:—

*Notes on the Examination of Preserved Meats, etc.*, by OSMAN JONES, F.I.C.

*Titanium in Nile Silt*, by E. GRIFFITHS-JONES.

##### PATENTS IN 1922.

We think it will interest everyone to know that in spite of poor trade and unemployment in 1922, Messrs. Rayner & Co., patent agents, of Chancery Lane, London, inform us that there is an increase of more than 300 patent applications over 1921 the figures being about 35,500, standing next to the highest in record.

The subject of "Wireless Telegraphy" shows considerable increase in the number of inventions, and after this comes reinforced concrete building construction, which is greatly practised in these days,

and probably the matter of most general interest is that numerous patents have been taken in labour-saving devices for the household, and many lady inventors have come successfully into this important branch, but aviation patents have gone entirely out of favour and show a considerable decrease.

Recent months show a distinct inclination to increasing business in H.M. Patent Office, which should be an indication of better industrial times, as inventions nearly always precede improvements in commerce.

#### NOTICES OF BOOKS.

*Formulary of the Parisian Perfumer*, by R. M. GATTEFOSSÉ. 4th Edition. Pp. 85. Edition Parfumerie Moderne, No. 112, Route de Crénieu, Villeur Bannelez-Lyon (France).

The fourth edition of this excellent little handbook has just been published by the *Société Française de Produits Aromatiques*, and M. Gattefossé, whose association with the *Société* proves him an authority upon perfumes, has maintained his high standard. As the author explained in his preface, the work is one calculated to be invaluable to extensive manufacturers and lesser specialists alike. Part I. embodies the classification, extraction, and testing of essential oils and the concentration of flower juices; the principles of perfume composition; and exhaustive formulæ and lists of fixators and resindors. Part II. is more practical, and contains two recipes for eau de Cologne, three for dentifrices, and three for toilet lotions; as well as the components of cold cream, brilliantines, and cosmetics. Considering that the volume only comprises 82 pp., it is extraordinarily comprehensive. Not only does it cover a wide field, but the matter contained has been carefully selected and intelligently listed. If M. Gattefossé has erred at all in its compilation, it is by being a trifle too brief at the expense of coherency; although, perhaps, for purposes of rapid reference, this is an advantage.

J.M.

*Second Year College Chemistry and Second Year Laboratory Manual*, by WILLIAM H. CHAPIN. Chapman & Hall. 15s. and 7s. 6d.

The author's familiarity with the modern requirements of chemical students and the

more up-to-date methods of tuition is clearly evidenced by these two books, which have just been published for the first time. The former constitutes the theory—and beliefs, but upon rudimentary fact—of not built upon a meaningless mass of rules the course; the latter, the practice. Valuable suggestions as to procedure through the course have also been incorporated. But what appear with prominence are the chapters upon ionisation, osmotic pressure, radioactivity, and the periodic system. The last-mentioned is especially enlightening, but the other three could, perhaps, be extended with advantage, as could the section upon the determination of atomic weights, although the author has quoted several works dealing exclusively with these sections. The Laboratory Manual follows closely the theoretical treatise, and the pre-

scribed experiments are well chosen and lucidly explained. One important omission, however, is the application and modification of Avogadro's Law, dealing with gases at or near the point of liquefaction; and greater attention could have been given to ion migration under the influence of electric currents. The two books, used conjointly, would, without doubt, not only teach the student, but also compel him to feel that he has a *grip* upon his subject, inspiring him with confidence, and thus facilitating the learning-processes. This, to say the least, is a novel feature, as the majority of textbooks seem to be written diatribes of uninteresting facts and formulæ. The "tone" of the work is something unusual, and that alone should induce demonstrators to adopt it as a standard course. J.M.

LIESEGANG RINGS. I. SILVER CHROMATE IN GELATIN AND COLLOIDAL GOLD IN SILICIC ACID GEL.\*

By EARL C. H. DAVIES.

[Contribution from the Chemical Laboratory, West Virginia University.]

INTRODUCTION.

It is generally agreed that while the present theories regarding Liesegang rings may cover the broad features of this phenomenon they are quite inadequate to explain its many details, complexities and variations. To study this phenomenon further, I have

in the first place investigated the effect of gravity on the formation of bands of silver chromate in gelatin. In the second place, I have studied the formation of rhythmic bands of colloidal gold in silicic acid gel, since this presents an ideal opportunity for following changes in the sizes of the particles.

SILVER CHROMATE BANDS IN GELATIN.

*Effect of Gravity.*—An aqueous solution of silver nitrate was made containing 8.5 g. in 100 cc. The gel contained 4 g. of powdered gelatin, 0.12 g. of potassium dichromate, and 120 g. of water. The gelatin was boiled with the water and the dichro-

TABLE I.  
Rate of Diffusion at 0°.

Tube	Time in days.									
	7	14	18	20	25	27	32	34	39	46
	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.	Cm.
A right	6.40	9.00	} The two ends had met							
A left	6.40	9.00								
A' right	6.40	8.75								
A' left	6.40	8.75								
B	6.40	9.25	10.60	11.29	12.62	13.10	14.35	14.80	16.25	16.5
B'	6.40	9.25	10.60	11.27	gelatin frozen					
C upper	6.40	8.68	} The two ends had met							
C' upper	6.40	9.04								
C lower	5.97	8.16								
C' lower	5.97	8.40								
D	5.76	8.60	9.80		10.80	13.17		14.65		
D'	5.76	8.60	Gelatin frozen							

\* From "The Journal of the American Chemical Society," December, 1922.

mate for a few minutes on a water-bath until solution had taken place, and the solution was then filtered into tubes. After it had solidified (standing over-night) and had been left in the ice-room at 0° for about 2 hours, the tubes were arranged as follows: A and A' were horizontal with silver nitrate contact at both ends; B and B' were horizontal with silver nitrate contact at one end; C and C' were vertical with silver nitrate contact at both ends; D and D' were vertical with silver nitrate at the lower ends; E and E' were vertical with silver nitrate contact at upper ends.<sup>1</sup>

The results given in Table I. show that diffusion is slowest when it operates against gravity (Tube D), and that hydrostatic pressure may partially counterbalance gravity (Tube C, lower).

After the 18th day the tubes were removed from the ice-room while observations were made at room temperatures and with varying light, either artificial or sunlight. Hence the results previous to the 18th day are most satisfactory. After that elapsed time all tubes were removed for the same length of time and subjected to practically the same light and heat conditions.

*Preliminary Bands.*—It seems from observations so far recorded that in the case of silver chromate in gelatin the method of ring formation is: first, the silver nitrate diffuses into the gelatin and gives what seems to be an opaque region which in reality consists of small opaque bands. These preliminary bands have not been observed in the earlier stages of diffusion. Tube B' at 13.5 to 15 cm. from the surface of entrance of the silver nitrate had 28 bands. Tube D had 16 bands at 12.8 to 13.8 cm. from the point of the beginning of the silver nitrate penetration. Tube E' had 26 opaque bands at 10.5 to 11.5 cm. from the surface. From this point it appears that there is a tendency for the opaque bands to be closer together in the earlier stages of diffusion and to be farther apart as the distance from the surface of initial diffusion increases. It is, therefore, not unlikely that this formation of preliminary bands extends to all portions of the tube, but that the bands are at first so close that they seem to merge.

<sup>1</sup> Data for E and E' were not given in Table I. because the silver nitrate had not the same strength as that used in the other tubes.

In the case of silver chromate in gelatin the reaction as carried out in a test-tube would be,  $K_2Cr_2O_7 + H_2O + 4AgNO_3 = 2KNO_3 + 2Ag_2CrO_4 + 2HNO_3$ . We are not dealing simply with silver chromate, and it is a well-known fact that electrolytes have a profound effect on gels. They not only influence the rate of imbibition of water, but also tend to produce peptization. As the gelatin gel ordinarily used is not as dilute as possible we know that it is capable of absorbing more water. The presence of nitric acid would disturb the layer of gelatin where it is produced. There is a similar change in rate of imbibition when a base is one of the products. The potassium nitrate and nitric acid have the greatest concentration at the layer of reaction between the potassium dichromate and silver nitrate. From microscopic observations it appears that at least at 0° some of the potassium nitrate is crystallised simultaneously with the small particles of silver chromate. The nitric acid is more soluble, and hence, according to Fick's law, diffuses faster than the potassium nitrate because it is potentially more concentrated.

It is to this unequal rate of diffusion that we attribute the preliminary bands. The groups of silver chromate-potassium nitrate "crystals" are gradually broken up as the potassium nitrate diffuses away and the silver chromate particles become larger because of the oncoming silver nitrate. Hence the small bands lose their identity and the larger band is formed. Below the small band the silver nitrate and nitric acid and some potassium nitrate are diffusing into the potassium dichromate. Of course, the potassium dichromate is diffusing "up" but because of its low concentration the rate of diffusion is low.

#### COLLOIDAL GOLD IN SILICIC ACID GEL.

*Light a Factor in Formation of Rhythmic Bands.*—To ascertain the effect of periodic illumination in the production of bands, I have carried out the following experiments, using colloidal gold in silicic acid at the concentrations suggested by H. N. Holmes,<sup>2</sup> who apparently carried out his experiments in changing light.

Tubes gave no bands either at 0° or at room temperatures when covered, light-

<sup>2</sup> Holmes, *Jour. Amer. Chem. Soc.*, 1918 XL., 187.

tight, with black paper and placed in a dark room even after 9 days. Instead, the gold precipitated in sparkling yellow particles. A band of about 1.5 cm. width was formed in these tubes by removing the black paper and exposing them to the light from a projection lantern for an hour. The band did not start as a fine line and then gradually grow; rather, it began as a faint colour throughout the entire region, becoming gradually more intense by longer exposure to the light until it reached a maximum at which all the gold adsorbed by the fibrils in this region had been precipitated. The colour was lighter at the top of the band and most intense near the bottom. Below the coloured zone, yellow crystals of gold could be seen for a distance of 8 to 9 mm.

Second, slits were cut in the black paper in such a way as to expose 2 mm. cover 8 mm., expose 2 mm., etc., throughout the length of a tube. This tube was placed in the dark room at a distance of 14 cm. from an 80-watt, 110-volt Mazda light. Slightly green colloidal bands developed at the openings after 9 days, and at each opening there were distinct yellow bands of gold crystals.

Third, a similar tube which had been in the dark at 0° for 6 days showed no bands at the openings. When this tube was exposed to the strong light of the projection lantern for a few minutes, bands developed at 2 of the openings in the same region as in the case of a tube which had been handled exactly similarly, except that it had no protection from the light of the lantern. Between these openings the bands did not form, although the tube was in the strong light for 1 hour. This tube was then put in the dark for 7 more days at 0°. The black slit paper was then entirely removed and the tube put in front of the lantern for 3 hours. There was a slight blue colour developed in the 8 mm. zone between these 2 bands. From the faint colour of this blue it was apparent that the light is not the only factor in promoting the band formation of the gold. There must also be proper concentrations of the oxalic acid and the gold chloride. The sodium sulphate is not included because it is presumably uniformly distributed.

Hence it seems that the molecular gold adsorbed by the walls is in some way at first protected from immediate precipitation

by the oxalic acid. It is probably oriented.<sup>3</sup> After a time such gold is gradually precipitated in the dark, but not in bands. At some other concentrations bands may be obtained in the dark; but so far I have observed no tendency for the gold to form in bands in silicic acid except under more or less periodic light changes. For example, E. Küster<sup>4</sup> found under certain conditions, in the case of bands of silver chromate in gelatin, that when the silver nitrate had diffused into the gelatin in the dark there was an evenly distributed precipitate, but when the diffusion area was exposed to light rhythmically, that is, alternate exposure (25 minutes) and darkness (45 minutes) the precipitate took the characteristic ring formation. I have obtained just as good bands of silver chromate in the dark as in the light, both at 0° and at room temperature of about 20°.

*Two-phase Character of Silicic Acid Gel.*—It seems that the "protected" gold chloride, which we have assumed to be adsorbed by the more solid portion of the gel cells, gradually diffuses away and is precipitated if the band is not started by the light, or the peptizing and imbibition action of the products of reaction. It is because of this migration and precipitation that the null spaces are formed.

When in the dark or in mild light there is a rather broad band which forms at the top of the silicic acid layer. This band was in some cases reddish-purple in transmitted light and yellow in reflected light. Below this there were sparkling, yellow crystals of gold. These latter precede the usual bands. Observed with a powerful Tyndall cone it is seen that the particles of gold are most numerous just beneath the band. They become relatively fewer until they cease to appear at a distance of about 8 to 9 mm. Then a band begins to form in the region already best filled with the larger particles of gold. The band owes its formation to the condensation of the molecular gold to the size of colloidal particles. Much of the gold has already been precipitated as microscopic particles. Hence in the formation of these bands there comes a time when there

<sup>3</sup> For discussion of the subject of molecular orientation see Harkins, Davies and Clark, *Jour. Amer. Chem. Soc.*, 1917, XXXIX., 541.

<sup>4</sup> Küster, *Kolloid-Z.*, 1913, XIII., 192.

is a considerable accumulation of the products of reaction, hydrochloric and carbonic acids. Also the concentration of the gold chloride becomes quite small, due to the previous precipitation of the microscopic particles. The whole experiment behaves as would be expected if the gold chloride were held in the gel in two ways. First, some of it is most free to move and forms the larger particles. Second, the accumulation of the products of reaction affects the "protective" coating on the other gold chloride molecules so that they are attacked by the oxalic acid. It would seem that these colloidal particles which form the bands must likewise be protected by the gel, as they remain unaffected by further diffusion of the electrolytes. This is what might be expected if we had films of the solid gel and pockets of the amorphous gel. W. Moeller<sup>5</sup> has observed such a formation in the case of gelatin, where he finds fibrils of  $\alpha$ -gelatin imbedded in amorphous  $\beta$ -gelatin.

However, the structure of the gel is not the only factor. Many experiments on band formation have been performed where gel was replaced by solids, as sand, sulphur, etc. There is also in these cases a possibility that an oriented adsorption of one of the reacting substances by the solid plays an important part. Some of the precipitate is, in nearly all cases, of a preliminary nature. It may be scattered, as in the case of gold, or in preliminary bands, as in the case of silver chromate in gelatin. These preliminary particles may sometimes be later partially converted into colloids by the excess of electrolytes but in the case of gold there seems to be no such tendency. The gold originally precipitated as blue remains blue, the red remains red. This shows that it is formed in protective coats of the gel. Otherwise we might expect the red particles to enlarge gradually and become blue as more of the diffusion takes place. The molecular gold in the fibrils forms the bands. The gold chloride in the amorphous portion of the gels forms the granules.

In all the bands of gold observed, the red has formed first where it has formed at all. In the region in which it is formed we have relatively large concentrations of oxalic acid as compared with the small amount of adsorbed gold. After a red band, the blue

forms. Under this same red band relatively large amounts of the yellow gold have been observed for a distance of 8 to 9 mm. beyond it. Hence, where the blue bands form there are relatively large amounts of the products of reaction, hydrochloric and carbonic acids, with relatively high concentration of adsorbed molecular gold. Under the latter conditions we should have greater tendency for adsorption of the oxalic acid with more of the "protected" molecular gold collecting in each "protected" colloidal particle.

*Effect of Temperature.*—Upon a study of the literature on Liesegang ring formation one is impressed by the small attention paid to the effect of temperature. Experiments have nearly always been carried out at room temperatures. Yet it is recognised that the elasticity of gels<sup>6</sup> is directly related to the formation of Liesegang rings. In the present experiments with silver chromate in gelatin, the bands were closer when made at 0° than when formed at room temperatures. Particularly in the case of gelatin should studies be made at different and regulated temperatures. Thus the ordinary gelatin gels melt between 25° and 29°, depending upon the concentration. When working at room temperatures with a 4 per cent. gelatin gel (m.p. about 26°), we are very close to the limit of non-elasticity. When we lower the temperature to 0° we have lowered the distance from the melting point by several hundred per cent. Therefore, we have greatly affected the elasticity and may expect marked influence on ring formation. At lower temperatures, the rate of diffusion is also lessened. It is doubtful whether as low a temperature as 0° is desirable, but it is certainly advisable to work at a uniform temperature not too close to the melting point of the gel. With the silicic acid there is not the difficulty of melting at higher temperatures. In fact it seems best many times to work at higher temperatures; but here also conditions of light and heat should be carefully regulated if the observations are to be more than qualitative.

*Conclusion.*—The oriented adsorption in the gel or porous solid of the reacting substances as well as the products of reaction have not received the attention which they deserve. On looking through the literature we find that the concepts, which existed

<sup>5</sup> Moeller, *Kolloid-Z.*, 1916, XIX., 205-213.

<sup>6</sup> See Hatschek, *ibid.*, 1914, XIV., 115-22.



prior to our knowledge of colloids, are carried over to explain facts which are clearly related to the phenomena of colloidal. Thus we read statements to the effect that "the ions diffuse toward each other until the solubility product is exceeded." It is not clear how this applies to the formation of bands which consist altogether of colloidal particles. The colloidal conception would be that a number of molecules, in some cases about 100 as for the usual colloidal silver, are congregated into a particle of rather definite size. If too many of the molecules collect on one "crystal" we have the usual precipitate (in our case the yellow crystals of gold). Hence it is necessary to regulate the number of these gold molecules which are reduced in a "protective" coating or pocket of the gel. Thus we are not surprised that light, heat, peptizing electrolytes and the rate of diffusion all play important roles in regulating the formation of bands and the size of particles in those bands, and in case of colloidal gold the colour which The Svedberg<sup>7</sup> has shown is directly related to the size of particles.

*Forecast.*—It seems possible to predict that subsequent experiments will show that in many cases of Liesegang rings which occur in nature light will be found to be an important factor. This is because of the natural periodicity of sunlight. Diffusion takes place at night with perhaps chemical reactions. Then in the daytime the combined action of the light and the products of the reactions is to cause a band to form where the concentrations and the nature of the diffusion medium are suitable. Further experiments will be made, especially with silicic acid gel to determine the effect of light as a factor.

"Preliminary" bands of silver chromate were observed after the diffusion in gelatin had extended 10 to 12 cm. at 0°. The presence of these is attributed to the unequal rate of diffusion of the products of reaction. About 3 of these preliminary bands gradually form the nucleus of the final band; 26 such bands were observed in a space of 1 cm. These "preliminary" bands gradually lose their identity as the silver chromate is carried to the final band by the excess of silver nitrate.

Light is one of the most important variables in making rhythmic bands of gold in silicic acid. At the concentrations used no bands were formed in the dark at either 0° or room temperatures. Periodic variations of strong light and darkness produce bands in those regions in which there is still adsorbed molecular gold, excess of acid and suitable amounts of the by-products of the reaction. These by-products make precipitation in bands possible because they influence the tendency toward imbibition and peptization so that the gold is precipitated in "pockets" just large enough to give a colloidal dispersion. There is no fundamental difference between the bands of blue gold and those of red. Any combination of conditions which tend to precipitate the gold from the "fibrils" in relatively large "pockets" will produce blue bands. The red bands are made when the pockets are not so large. Rhythmic bands of silver chromate form in gelatin in the dark at 0° and at room temperatures.

*Silicic acid gel is a 2-phase system*; the gold chloride is held in the gel in two ways. Some of it is most free to move and forms the larger yellow crystals before the bands begin to appear. The remainder of the gold chloride seems to be more "protected" by the gel. Oriented adsorption takes place at the interface between "fibrils" of  $\alpha$ -gel and the amorphous  $\beta$ -gel. This oriented adsorption may set up a temporarily "passive" state, even where the adsorbed substance is not actually coated by a film of the gel. Such orientation can occur when solids such as alundum and sulphur are the mediums in which Liesegang rings are made.

At room temperatures gelatin gel is near its point of minimum elasticity. More experiments should be carried out with it at lower and uniform temperatures.

#### SUMMARY.

Gravity decreases the rate of diffusion upward during the formation of Liesegang rings of silver chromate in gelatin dichromate.

In conclusion the author wishes to express appreciation for the co-operation of W. B. Shirey and Professor Friend E. Clark of this Laboratory.

Morgantown, West Virginia.

<sup>7</sup> Ostwald, "Theoretical and Applied Colloid Chemistry," 1st ed., 1917, p. 60.

## THE USE OF MALIC, MALEIC AND FUMARIC ACIDS IN VOLUMETRIC ANALYSIS.\*

By N. A. LANGE AND HARRY KLINE.

[Contribution from the Chemical Laboratory, Case School of Applied Science.]

Malic, maleic and fumaric acids<sup>1</sup> are now available in large quantities and at comparatively low prices, and an investigation was, therefore, made to determine whether they might replace the more costly succinic acid<sup>2</sup> for standardising basic solutions. A. Astruc<sup>3</sup> has shown that when phenolphthalein is used as the indicator many of the dicarboxyl acids, including the acids mentioned above, behave as though they have 2 replaceable hydrogen atoms, whereas with methyl orange the end-point is uncertain. No methods of purification nor data of titrations were given for these acids.

In the experiments below, the sodium hydroxide solutions free from carbon dioxide were prepared in the usual manner by the addition of barium chloride, and then standardised against hydrochloric acid, the normality of which was determined by precipitation of silver chloride; the normality of the sodium hydroxide was also determined by titration with pure succinic acid.

**Maleic Acid.**—Commercial maleic acid was found to be too impure to use directly. The acid was, therefore, purified by crystallisation in four different ways: (1) a single crystallisation from water; (2) two crystallisations from water; (3) one crystallisation from 200 cc. of water to which had been added 4 drops of conc. nitric acid; (4) crystallisation as in (3) and then once more from pure water. After air-drying, the crystals were dried to constant weight over sulphuric acid or in an oven at 90° for 2 hours. Definite amounts of the acid were dissolved in distilled water, which was previously boiled to expel carbon dioxide and allowed to cool to about 50° before addition of the acid. In each case the standard sodium hydroxide solution was then added

until the end-point with phenolphthalein was obtained. The normality of the base against standard hydrochloric acid was 0.1087 N; 4 titrations with succinic acid gave an average value of 0.1087 N with an extreme variation of = 0.0001 N; the normality determined with 16 samples of maleic acid dried over sulphuric acid and varying in weight from 0.1696 to 0.2642 g. averaged 0.1088 N with an extreme variation of +0.0001 to -0.0003 N; titration with 4 samples of maleic acid dried at 90° and varying in weight from 0.1987 to 0.2339 g. gave an average value of 0.1087 N with an extreme variation of = 0.0001 N. It was found that maleic acid, after one crystallisation from water or from water with a few drops of nitric acid, will give results as accurate as obtainable with succinic or hydrochloric acids. Several determinations with samples of maleic acid dried at 105° and 120° showed that a small amount of maleic anhydride is formed; such samples after standing in the open air for 24 hours are hydrolysed, giving accurate results after drying again in a desiccator over sulphuric acid or in an oven at 90° and reweighing before titration.

**Fumaric Acid.**—Commercial fumaric acid was found to be too impure to use directly; any one of the four methods given above may be used to purify it. The normality of the base determined with 16 samples of fumaric acid dried to constant weight over sulphuric acid and varying in weight from 0.1280 to 0.4249 g., gave an average value of 0.1082 N with an extreme variation of +0.0003 to -0.0001 N; the normality of the base determined with 4 samples of succinic acid averaged 0.1081 N and with hydrochloric acid 0.1082 N. The results with fumaric acid dried for 2 hours in an oven at temperatures from 90-120° gave an average value of 0.1082 N with an extreme variation of +0.0002 to -0.0001 N. The results show that fumaric acid may serve as a standard in alkalimetry after one crystallisation from water, although a higher temperature of the solution must be maintained during the titration because of the lower solubility.

**Malic Acid.**—Malic acid is very soluble in water, and was therefore recrystallised by dissolving in hot acetone, filtering, and then adding carbon tetrachloride to the hot solution and allowing the acid to crystallise on cooling. The crystals were dried in air for about 24 hours and then dried in a desiccator over sulphuric acid for an equal length

\* From "The Journal of the American Chemical Society," December, 1922.

<sup>1</sup> U.S. pat. 1,318,631-2, -3.

<sup>2</sup> Phelps and Weed, *Am. J. Sci.*, 1908, XXVI., 138; *Z. anorg. Chem.*, 1908, LIX., 114.

<sup>3</sup> Astruc, *Z. anal. Chem.*, 1901, XL., 418; *Compt. rend.*, 1900, CXXX., 253.

of time, or for 2 hours in an oven at temperatures from 90° to 120°. The normality of the base determined with 4 samples of malic acid dried over sulphuric acid and varying in weight from 0.2071 to 0.2742 g., gave an average value of 0.1081 N with an extreme variation of +0.0001 N; the normality of the base determined with hydrochloric acid and with succinic acid was 0.1081 N; the determination with samples of malic acid dried at 90-120° gave an average value of 0.1082 N with an extreme variation of +0.0002 to -0.0001. It is evident that malic acid can easily be obtained pure, and because of its greater solubility would be more valuable as a standard than either maleic or fumaric acids.

Maleic and fumaric acids are oxidised by potassium permanganate according to the following equation:  $4 C_4H_4O_4 + 5O \rightarrow 3CO_2 + H_2O + HCOOH$ . Conflicting statements are made by previous investigators concerning the quantitative course of this reaction. This work was repeated, and it was found that although these acids may be used as standards for permanganate solutions, they are not as accurate nor as convenient as sodium oxalate. This is due to the low hydrogen equivalent of the acids which necessitates using very small samples with the consequent greater effect of any small errors in weighing and the difficulty of titrating boiling solutions. Titrations of malic acid were conducted in the same manner but the results were too variable and inaccurate to be of any value. Experiments with maleic or fumaric acid as titrating agent with 0.1 N iodine solution using starch as indicator did not give accurate results.

Attempts to standardise a 0.1 N ammonium hydroxide solution by titrating against known weights of malic, maleic, fumaric and succinic acids using either cochineal or methyl red as indicator were not successful. Although it is evident for theoretical reasons that a sharp end-point cannot be obtained in titrating a weak acid with a weak base, nevertheless conflicting statements have been made by previous investigators on the use of succinic acid in

the standardisation of ammonium hydroxide solution with cochineal as an indicator.<sup>5</sup>

#### SUMMARY.

It is evident that malic, maleic, and fumaric acids may be used with great accuracy as standards for sodium hydroxide solutions; it is further obvious that all 3 acids may be obtained in a pure form very readily, and all may be dried over sulphuric acid; malic and fumaric acids may be dried for 2 hours at temperatures from 90° to 120°; because of the formation of the anhydride, samples of maleic acid should not be dried above 100°. As standards in alkalimetry and acidimetry these acids, in the pure state, are as accurate as hydrochloric acid determined gravimetrically as silver chloride. The most serviceable of these organic acids are those most soluble in water—malic and maleic acids—although they are no more accurate than fumaric acid. Although maleic and fumaric acids may be used as standards for potassium permanganate solutions, they are neither as accurate nor as convenient as sodium oxalate for this purpose. Succinic, malic, maleic, and fumaric acids cannot be used as standards for ammonium hydroxide solutions; the last 2 acids cannot be used for iodine titrations.

Cleveland, Ohio.

<sup>5</sup> Phelps and Hubbard, *Z. anorg. Chem.*, 1907, LIII., 361; *Am. J. Sci.*, 1907, XXIII., 211. Peters and Sauchelli, *Am. J. Sci.*, 1916, XLI., 244.

### A PRELIMINARY STUDY OF ZIRKITE ORE.

By J. G. THOMPSON.

(From "The Journal of Physical Chemistry," New York, December, 1922.)

(Continued from Page 31.)

The partially purified carbide apparently had a higher melting point than the oxide product with the same relative composition. This was shown in the runs in which the ore melted and formed a pool under the arc, the pool solidifying as soon as more carbon was added. In order to use the

<sup>4</sup> Perdrix, *Bull. soc. chim. Paris*, 1900, [3] XXIII., 645. Clarke, *Am. Chem. J.*, 1881, III., 201. Micko, *Z. anal. Chem.*, 1892, XXXI., 465. *Z. allgem. österr. Apotheker Ver.*, 1891., XXX., 197.

carbide as a refractory, however, it would be necessary to protect it from oxidation. The black carbides all burned readily in the air to form light, fluffy oxides. Heating the powdered carbides to dull redness is sufficient to start the oxidation, which then proceeds slowly but persistently.

The data show that some titanium was also eliminated but no iron, there being an apparent increase in the amount of the last impurity. This apparent increase in the iron content, especially in the case of Run 18, is due to the difficulties encountered in analysis. The samples of furnace products must be pulverised for analysis, and, since the amount of silicon present is of primary importance, grinding such abrasive material in an agate mortar is out of the question. The only other method available was the use of a cast-steel bucking board, which resulted, naturally, in contamination of the samples. In view of the time required for analysis it was not considered advisable to grind additional samples in an agate mortar for the determination of iron. From a consideration of the data in Table III., therefore, one may safely conclude only that little if any iron was eliminated under the conditions of experiment.

Other runs were made in which sodium chloride was added to the charge of ore and coke to aid in the removal of iron, but curiously enough no iron was eliminated in this way. It is possible that the rapid attainment of the high temperature under the arc decomposed the chloride before it could be volatilised away.

Since the treatment in the electric furnace was not successful in eliminating the iron, other means of accomplishing this end were sought.

#### EXPERIMENTS ON THE REMOVAL OF IRON.

Different samples of the various electric furnace products all showed magnetic properties, due presumably to the presence of iron either as carbide or alloy. Accordingly attempts were made to use these magnetic properties as a basis of separation of the iron, but the attempts were not successful. The magnetic portions contained approximately half of the zirconium and the non-magnetic portions contained appreciable amounts of iron.

Attempts were next made to remove the iron by leaching with 5 per cent. sulphuric

acid.<sup>35</sup> Both the carbide and the corresponding oxidised products of the electric furnace runs were leached with hot and with cold 5 per cent. sulphuric acid. The iron in the carbide appears to be more susceptible to leaching than is the iron in the oxidised material; but, even in the case of the carbide, less than half of the iron could be removed in this way.

A series of experiments was next carried out on the removal of iron by treatment of the carbides or mixed oxides with chlorine<sup>36</sup> at both low and high temperatures. The experiments were carried out in a small, horizontal, tube furnace, and the frequent clogging of the apparatus by the volatile products of the reactions, especially at high temperatures, showed plainly that a furnace of special design is essential for investigation of this possibility. Nevertheless, results were obtained which indicated that iron may be removed in this way from zirconium carbide at low temperatures, and, at high temperatures, from zirconium oxide from which silicon had been largely eliminated in the arc furnace. It would seem, therefore, that a fairly pure zirconia for refractory purposes might be made from crude zirkite ore by eliminating in an electric furnace as much as possible of the silicon and by following this by treatment with chlorine or phosgene<sup>37</sup> to remove the iron.

This investigation is admittedly incomplete in many ways. The limited time at our disposal and the difficulty of, and the time consumed by, the analytical work involved, may be offered as an excuse. It is hoped, however, that attention will be called to the problem of large-scale purification of zirconium oxide, so that the latter may become more generally available as a refractory material for very high temperatures. A summary of the results obtained follows:

#### SUMMARY.

- (1) Ninety to ninety-five per cent. of the silicon may be removed from siliceous zirkite ore by heating a mixture of ore carbon to a temperature greater than 2,220° C. in an electric furnace.
- (2) The best results appear to be ob-

<sup>35</sup> Barton: *loc. cit.*

<sup>36</sup> Phillips: *loc. cit.*

<sup>37</sup> Baskerville: *Science*, 1919, L., 443.

tained by feeding into an arc furnace a mixture of ore and coke, the amount of carbon being approximately that required to transform only the silicon to the carbide.

(3) The existence of stable double carbides of silicon and zirconium, or of solutions of silicon carbide in solid zirconium carbide, has been suggested as an explanation of the incomplete removal of silicon when carbon in excess of that required to form only silicon carbide is used.

(4) It is suggested that zirconia sufficiently pure for refractory purposes might be obtained from zirkite ore by removing the silicon in an electric furnace and following this treatment with chlorine or phosgene to remove the iron.

(5) Attention has been called to the refractory properties of zirconium carbide and the factors which limit its use.

(6) Methods of analysis of zirconium compounds have been reviewed briefly and a modified scheme of analysis has been outlined for the determination of zirconium and the three major impurities, silicon, iron, and titanium.

*Cornell University, 1920.*

## THE ODOUROUS CONSTITUENTS OF APPLES. II. EVIDENCE OF THE PRESENCE OF GERANIOL.\*

BY FREDERICK B. POWER AND VICTOR K. CHESNUT.

[Contribution from the Phytochemical Laboratory of the Bureau of Chemistry, United States Department of Agriculture.]

In a previous communication<sup>1</sup> it was shown from the results of a somewhat extended investigation that the odourous constituents of the apple consist chiefly of the amyl esters of formic, acetic and caproic acids, with a very small amount of the caprylic ester and a considerable proportion of acetaldehyde. It has, however, been noticed by us and remarked by others that, in addition to the odour imparted by the

above-mentioned esters, some particularly choice varieties of the apple have a distinctly rose-like odour. We had furthermore observed in the previous investigations that when the esters contained in a concentrated distillate from apple parings were hydrolysed, the alcoholic product so obtained possessed an odour which was more pleasant than that of pure amyl alcohol, although the presence of the latter in predominating amount was completely established. It was thus evident that the amyl alcohol was accompanied by a relatively small proportion of another substance of alcoholic nature, but the amount of material available did not permit of its identification. The odour of the above-mentioned hydrolytic product had suggested the possibility of the presence of the aliphatic terpene alcohol geraniol,  $C_{15}H_{18}O$ , which is known to possess a rose-like fragrance, and the correctness of this supposition has been confirmed by the results of the present investigation.

### EXPERIMENTAL.

In order to accomplish the particular purpose in view it was desirable to employ one of the most fragrant varieties of the apple, and the well-known McIntosh apple was consequently selected. The fruit was obtained from the Boston market and, as in the previous investigations, only the parings were used. The separation of the thin rind was accomplished by means of a machine, which was so adjusted as to remove only a very small portion of the white substance of the apple. By some preliminary weighings it was found that the proportion of the fresh parings to the entire fruit was approximately 12.5 per cent.

### EXTRACTION OF THE ESSENTIAL OIL

*From Apple Parings.*—A quantity (31.75 kg.) of the apple parings, without any further addition of water, was subjected to distillation with steam and 76 litres of distillate collected. The entire distillate was then cohobated in a current of steam until the odourous constituents were finally contained in a volume of 0.5 litre. This concentrated liquid was extracted five times successively with ether, the ethereal liquids being then dried with anhydrous sodium sulphate, and the greater part of the solvent removed by distillation. The remaining liquid was allowed to evaporate spontaneously in a small, tared flask, until the residue was of practically constant weight.

\* From "The Journal of the American Chemical Society, December, 1922.

<sup>1</sup> Power and Chesnut, *Jour. Am. Chem. Soc.*, 1920, XLII., 1509.

A pale yellow, somewhat viscid oil was thus obtained, which had a fragrant and characteristic apple-like odour. The amount of this product was 0.6977 g., which corresponds to 0.0022 per cent. of the apple parings, or about 0.00027 per cent. of the entire fruit. This essential oil gave very slight reactions for acetaldehyde and for furfural, and was similar in its general characters to the analogous products from other varieties of the apple which the present authors have previously described.<sup>1</sup>

*From Apple Pulp.*—In order to ascertain whether any appreciable amount of essential oil is contained in the fruit after the removal of the rind, an experiment was conducted with a small quantity of the same lot of McIntosh apples as that used for the main investigation. The fruit, after being pared by means of a machine, was cut into quarter sections, and the core and seeds completely removed. This material, amounting to 5 kg., was then distilled in a current of steam, and about 3 litres of distillate collected. The slightly opalescent, neutral liquid was less fragrant than the distillate from the parings, the odour somewhat resembling that of a baked apple, and it gave a strong reaction for acetaldehyde. The entire distillate was cohobated in a current of steam until the odourous constituents were contained in a volume of 0.5 litre. This concentrated liquid was completely extracted with ether, the ethereal liquid dried with anhydrous sodium sulphate, and the solvent removed as previously described. A pale yellowish oil was thus obtained, which amounted to 0.0614 g. or 0.000123 per cent. of the weight of material employed. It was evident from this result that the odourous constituents of the fruit are contained most largely in the outer portion or rind. This essential oil had a pleasant, apple-like odour and gave no reaction for furfural.

#### HYDROLYSIS OF THE ESTERS CONTAINED IN THE APPLE DISTILLATE.

For the purpose of obtaining further information respecting the esters contained in the apple, and especially to ascertain whether geraniol could be detected in them, a considerable quantity (36.85 kg.) of apple parings was employed. The fresh material was brought into a still and, without any further addition of water, subjected to distillation in a current of steam. About 76 litres of distillate was collected, and this

was subsequently cohobated with steam until the odourous constituents were contained in a volume of 1 litre. To this concentrated liquid, which was contained in a flask provided with a reflux condenser, 20 g. of pure sodium hydroxide was added, and the whole kept in a state of active ebullition for 2 hours. It had then acquired a deep yellow colour and become turbid, owing to the separation of aldehyde resin. After cooling, the alkaline mixture was distilled, and 0.5 litre of distillate collected. This liquid, which had a pleasant odour and contained some oily drops, was extracted 5 times successively with pure, aldehyde-free ether, the united ethereal liquids were dried with anhydrous sodium sulphate, and the greater part of the ether was removed by distillation. The residual liquid was then brought into a small pressure flask, in which it was allowed to evaporate spontaneously until all the ether had been removed. A yellowish oil was thus obtained, which amounted to 0.3641 g. and, therefore, represented 0.00098 per cent. of the weight of the apple parings employed. This oily liquid possessed a distinct odour of amyl alcohol, but the presence of a more fragrant substance was also indicated.

#### OXIDATION OF THE ALCOHOLS OBTAINED BY HYDROLYSIS. FORMATION OF VALERIC ACID AND CITRAL TOGETHER WITH ACETONE AND LEVULINIC ACID.

To the small amount of the above-mentioned hydrolytic product contained in a pressure flask there was added, while being kept cool, 10 cc. of a chromic acid mixture<sup>2</sup> and, after closing the flask, the whole was heated on a water-bath at a temperature of about 90° for 15 minutes, with occasional agitation. After being allowed to cool, the mixture was diluted with water and extracted 5 times successively with freshly distilled, aldehyde-free ether. The united ethereal liquids were washed thrice with water, dried with anhydrous sodium sulphate, and the greater part of the ether was removed by distillation. The liquid was then transferred to a small distilling flask in which the remaining ether was allowed to evaporate spontaneously, the last portion of the solvent being removed by aspiration. A small amount of an oily liquid was thus

<sup>2</sup> *J. prakt. Chem.*, 1892, XLV., 599.

obtained, to which some water was added, and the product then distilled in a current of steam. Two fractions of distillate, amounting to 5 cc. and 25 cc. respectively, were collected. The first portion was strongly acid, contained on the surface a small globule of yellowish oil, and possessed a distinctly lemon-like odour together with the odour of valeric acid.

*Occurrence of Geraniol in the McIntosh Apple.*—A very small portion of the above-mentioned acid distillate gave with Schiff's reagent a deep purplish colouration, similar to that yielded by citral and quite different from the colour produced by the ordinary aliphatic aldehydes. It is also rapidly reduced an ammoniacal solution of silver oxide. These results, together with the odour of the original hydrolytic product, clearly indicated the presence in the latter of a small amount of geraniol. Inasmuch as the further oxidation products of geraniol or citral are acetone and levulinic acid, the probable formation of small amounts of these substances was also considered. About 0.5 cc. of the above-mentioned 5 cc. of distillate was consequently tested for acetone by means of the iodoform reaction; distinct crystals of the latter substance were obtained.

In order to obtain evidence of the presence of levulinic acid, the amount of which would be extremely small, consideration was taken of its ketonic character and capability of yielding iodoform. The following method was therefore employed for its detection. After the complete distillation of the oxidation product with steam, as above described, the liquid remaining in the distillation flask was extracted thrice with ether, the united ethereal liquids were dried with anhydrous sodium sulphate, and the greater portion of the ether was removed by distillation, the residual liquid being allowed to evaporate spontaneously. A very slight amorphous residue was thus obtained which was heated for a short time on a steam-bath in order to expel any trace of volatile substance. When cold it was treated with a little water, the filtered liquid made slightly alkaline with sodium hydroxide and a few drops of iodine solution added, when a separation of iodoform soon ensued.

The results of the above tests will be seen to have given quite definite indications of the formation of small amounts of both acetone and levulinic acid, together with citral, by the oxidation of the above-

described product of hydrolysis, and they are therefore believed to afford satisfactory evidence of the presence in the latter of geraniol.

*Occurrence of Amyl Esters in the McIntosh Apple.*—Although a previous investigation by the present authors<sup>1</sup> had established the fact that the odorous constituents of certain varieties of the apple consist chiefly of various amyl esters, their presence in the McIntosh apple has now also been determined. As already noted, the product obtained by the hydrolysis of the concentrated aqueous distillate possessed a distinct odour of amyl alcohol, and when subjected to oxidation by chromic acid, with subsequent extraction by ether and distillation of the ethereal extract in a current of steam, it yielded a strongly acid liquid containing some oily drops. It was also observed that the odour of this liquid indicated the presence of both citral and valeric acid.

In order to establish the identity of the last-mentioned substance, the first portion of the aqueous distillate, which had responded to the tests for both citral and acetone, was made alkaline with baryta, when the oily drops almost completely disappeared and the lemon-like odour of the liquid became much more pronounced. The two portions of distillate were then united, and the alkaline liquid was extracted thrice with pure ether. The ethereal liquids, after being washed with a little water and dried with anhydrous sodium sulphate, were allowed to evaporate spontaneously, when a slight residue was obtained which possessed a distinct lemon-like odour. When this residue was shaken with sensitized Schiff's reagent it soon developed the characteristic purple colour produced by citral.

After extraction with ether, as above described, the alkaline liquid was concentrated, filtered, the excess of baryta removed by carbon dioxide, and the liquid, which was now perfectly neutral, again filtered and concentrated. On the addition of silver nitrate it yielded a small amount of a white, curdy precipitate, which was collected, dried, and analysed.

*Analysis.* Subs., 0.0685: Ag, 0.0348. Calc. for Ag, C<sub>5</sub>H<sub>9</sub>O<sub>2</sub>: Ag, 51.7. Found: 50.8.

A trace of the silver salt, when moistened with dil. sulphuric acid, developed a distinct odour of valeric acid. These results

may, therefore, be considered to confirm the presence of amyl esters in the particular variety of apple now examined.

Although the present investigation of McIntosh apples was conducted primarily for the purpose of determining the presence of geraniol, consideration was also given to all the constituents that had previously been found in other varieties of the fruit. The methods adopted for the separation and identification of these constituents, with the exception of the oxidation products of the alcohols, were practically the same as those previously employed, and therefore require no further description. The results, with the following slight exception, were in complete accordance with those previously obtained. A very small amount (0.06 g.) of a paraffin hydrocarbon, which separated from the original distillate of the apple parings, was obtained in the form of minute, acicular crystals, melting quite sharply at 54°. It differed in appearance from the analogous substance previously obtained from the Ben Davis apple, which melted at 63°.

#### CONCLUSIONS.

An examination of McIntosh apples, which represent a particularly fragrant variety of the fruit, has confirmed the results of a previous investigation that the odorous constituents of the apple consist chiefly of amyl esters, and it has also afforded further information respecting the substance which imparts to some apples a distinctly rose-like odour. Although the proportion of this substance, even in the McIntosh apple, is extremely small, it has nevertheless been possible to determine with a considerable degree of certainty that it consists of the aliphatic terpene alcohol geraniol  $C_{10}H_{18}O$ . The evidence for this conclusion may be adduced from the fact that by the hydrolysis of the esters of the apple a product was obtained which possessed, in addition to the odour of amyl alcohol, a rose-like fragrance, and that by the oxidation of this product it yielded, besides valeric acid, a substance which had the characteristic odour and other properties of the aldehyde citral. At the same time the formation in very small amounts of the further oxidation products of geraniol or citral, which are acetone and levulinic acid, was decisively indicated. It is probable that geraniol, either in the free state or in the form of esters, is contained in varying amounts in all the numerous

vareties of the apple, although to the greatest extent in those which possess its distinctive odour.

Washington, D.C.



This list is specially compiled for the *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

#### Latest Patent Applications.

- 34891—Etablissements Poulenc Freres.—Manufacture of hydroxylated aliphatic arsenic acids. Dec. 21.  
 34846—Madel, G.—Roasting or calcining ores. Dec. 21.  
 34479—Parrish, P.—Distillation of ammoniacal liquors. Dec. 18.

#### Specifications Published this Week.

- 189475—Helps, G.—Manufacture of gas.  
 189542—Ironside, T. G.—Process of distilling oil shales, coal, and other carbonaceous materials, and apparatus thereof.  
 189700—Dutt, E. E.—Process for the extraction of titanium dioxide and vanadium salts from bauxite.  
 189701—Willis, N. E.—Clarifying of solvents and oils.  
 184153—Chemische Fabrik Weissenstein Ges.—Manufacture of hydrogen peroxide.  
 187232—Chemische Fabrik in Billwarter Vorm Hell & Sthamer Akt Ges and Hasenclever.—Production of chrome-alum.  
 164731—Leibreich, Dr. E.—Process for separating out metallic chromium.  
 189834—Dandridge, A. G., and Thomas, J.—Manufacture of dyestuffs of the anthraquinone series.  
 168902—Norsk Hydro-Elektrisk Kvatlstof-Aktieselskab.—Production of ammonia from nitrogen and hydrogen.  
 181385—Jacobson, B. H.—Process of making anhydrous metallic chlorides.

#### Abstract Published this Week.

*Synthetic Drugs*.—Patent No. 188127.—Messrs. Cassella & Co., Ges. L. of Frankfort-on-Main, Germany, have patented in this country a process for the preparation of Acridinium salts of fatty acids. The product is prepared by treating acridinium salts of mineral acids with salts of fatty acids of high molecular weight. Examples are given of the preparation of 3:6-diamino-10-methylacridinium stearate, 2:7-dimethyl-3:6-diamino-10-methylacridinium stearate, and 3:6-diamino-10-methylacridinium palmitate. The products are soluble in fats and oils and suitable for therapeutic use.

Messrs. Rayner & Co. will obtain printed copies of the published specifications, and forward on post free for the official price of 1s. each.



# THE CHEMICAL NEWS,

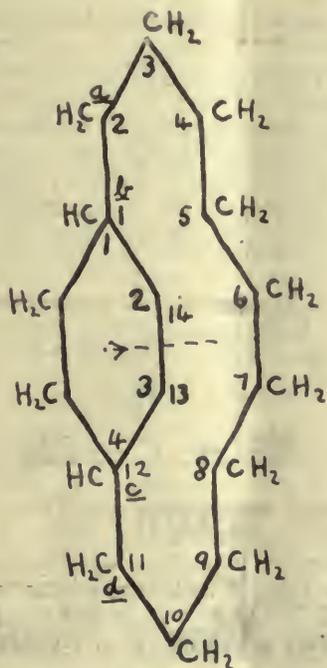
VOL. CXXVI. No. 3276.

## A NEW SYSTEM FOR THE LINEAR REPRESENTATION OF THE STRUCTURE OF ALL ORGANIC COMPOUNDS.

By T. SHERLOCK WHEELER, B.Sc.,  
A.R.C.Sc.I., A.I.C.

(Continued from Page 35.)

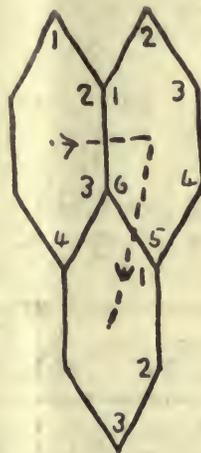
Bridges are shown as chains linked to a ring in two positions, just as two positions at which rings are fused are shown. X. is Al. VI. 2, 3 VI. 2, 5 III. (N-2, 2-Me). It is to be noted that the numbering of the bridge is from the common carbon first given, in this case from "2." Bridged rings can also be considered as two ring systems fused in ortho, meta, para and other positions. The rules given for the ortho-hold for the meta- and para-fused rings, except that it is the extreme (tertiary) common carbons that are given in passing from one ring to another; the numbering of the second ring begins at the extreme left-hand common carbon. Some



XI

meta-fused rings are known; with the exception of bridged rings para-fused rings are unknown to the present. Compounds of the type of XI. do not seem impossible, especially if the six membered ring shown be aromatic, as then the valencies "ab" and "cd" are fixed in a plane. XI. is Al. VI. 1, 4 XIV. The second ring in para-fused compounds can usually lie equally well on either side of the first. Adherence to the rule that the left-hand common carbon is given first is sufficient to show on which side of the first ring the second one lies. Al. VI. 4, 1 XIV. would be XI. with the second ring on the other side of the first. In the example given, these two compounds would be identical, but cases could occur where that would not be so. The same holds for rings fused in any position, but the question is not likely often to arise.

The same symbols preceded by Ar. and Al. always represent similar systems except in one case. That is when a ring has two adjacent sides common to two other rings. XII. is Ar. VI. 2, 3 VI. 5, 6 VI., and valency considerations show that the first and the third rings must be fused as shown. But the consistent interpretation of Al. VI. 2, 3 VI. 5, 6 VI. is XIII., and not XII.

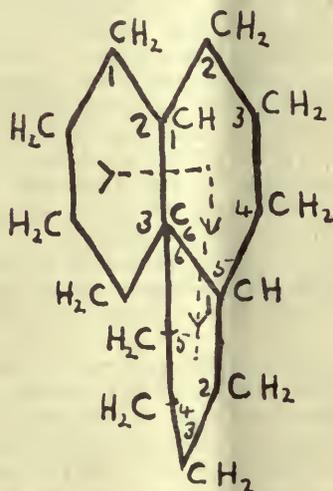


XII

fully reduced. To describe the latter, the third ring is considered as a chain joining the second and the first, and it becomes Al. VI. 2, 3 VI. 5, 4 V. Any alicyclic compound can be dealt with in this way. It

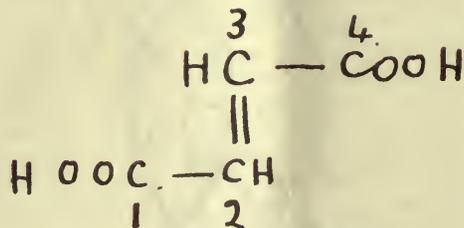
will be noted how the index identifies the ring to which we return.

Since aromatic rings are seldom written with the fourth bond, there is no need to indicate which method of disposing of it is being used. Should it be necessary to do this, a prefix "Cn" for the centric, or "K"



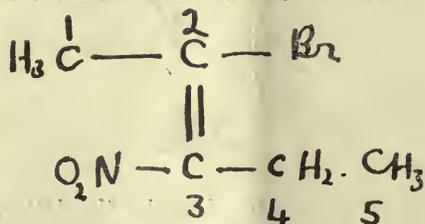
### XIII

for Kekulé's method, can be employed. If it be desired to have any conjugated bonds represented on Thiele's system, the prefix



### XIV

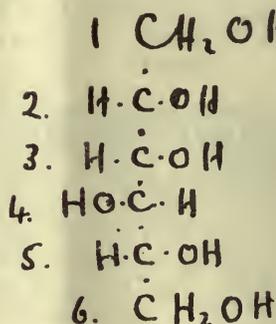
"Th" is placed before the ordinary symbol for them. "Cis," "trans," and such like stereo-chemical terms are to be used with



### XV

their present meanings. They are put in between the symbols of the groups or the elements to which they refer. XIV. is  $\overline{\text{IV}}$ . ( $1:4 = (\text{OH})_2$ ,  $1:4 \equiv (\text{O})_2$ ,  $\Delta^2$ , 1 trans 4). XV. is  $\overline{\text{V}}$ . (2-Br trans 3- $\text{NO}_2$ ,  $\Delta^2$ ).

Fischer's "+" and "-" system is used

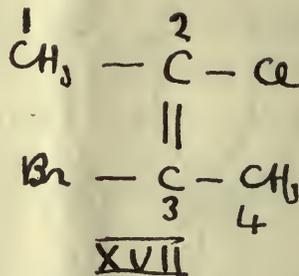


### XVI

for the sugars and such like asymmetric compounds. XVI. is  $\overline{\text{VI}}$ . ( $2:3:5 \equiv (\text{OH})_3$   
+ + - +

$4 - (\text{OH})$ ,  $1:6 = (\text{OH})_2$ , or VI. ( $1:2:3:4:5:6 \equiv (\text{OH})_6$ ). Cis and trans compounds can also be shown by the use of the same nota-

tion; XVII., e.g., is  $\overline{\text{IV}}$ . (2-Cl, 3-Br,  $\Delta^2$ ). Of course "+" and "-" then have not quite the same meaning in asymmetric and in stereo-chemical compounds, but the notation is convenient and no ambiguity is likely to arise. In compounds like the sugars, etc., the conventions as to the



graphical formula being written with the aldehyde group on top before the plus and minus rule is applied, etc., are adopted.

(To be Continued.)

## THE RARE EARTHS AND THEIR METALS.

BY JOHN MISSENDEN.

### I.—THE COMPOSITION OF THE RARE EARTHS.

(a) In view of the fact that so little has been known of the properties and reactions of many of the rare earth metals (and, accepting the periodic system for the classification of the elements as mathematically authentic, there is little doubt that others have yet to be discovered), and that the results of the majority of chemists differ to a more or less marked degree, it is small wonder that considerable differences of opinion prevail. The difficulties have not lain so much in the metals themselves as in their sources. The complexity of the so-called rare earths—their very composition, in the majority of instances, comprising more separate elements in both mechanical and chemical association than any other class of earth—demands so much care and precision in analysis, that only the most up-to-date methods of investigation can be called into use for the production of satisfactory and exhaustive data.

But the difficulties confronting modern researchers are not nearly so formidable as those faced by Klaproth, Berzelius, and Hisinger, Gadolin, Mosander, and a host of others. These chemists—whose investigations ran over a period from 1793 (or 1794) to the end of the nineteenth century—examining not only the actual earths themselves, but also (as, specifically, in the case of Mendeléeff, who will be dealt with later) daring to predict the presence of undiscovered elements, started upon a train of research which was, perhaps, one of the most difficult branches of chemistry. Certainly, it was (and still is) the most interesting of all the metal groups.

(b) Because the first of these mineral earths was discovered, according to the records dealing with that period, in Sweden, much of the credit for finding them is due to the professors and others studying in that country. Some idea of the arduity of their task can be gained by noting the dates which mark the intervals of bringing to light even the actual earths themselves, disregarding for a moment the separation

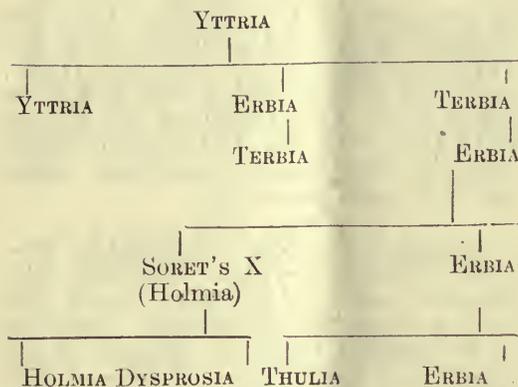
of the metals. For instance, six years elapsed—six years of strenuous work—between the discovery of *gadolinite* (1788), and *yttria* (1794), which formed part of its composition. *Ceria* (1803) was not split up until thirty-six years had elapsed; while *didymia* (1841) resisted analytical efforts for thirty-eight years.

(c) *Gadolinite*, then, discovered by Professor Gadolin, who came from Abo, the one-time capital of Finland, formed the basis of subsequent experiments. Referring to the works of Petersson, which are dated more than a century later, it is found that this mineral earth consists of, among other compounds: yttrium oxide,  $Y_2O_3$ , 45.3 per cent.; cerium sesqui oxide,  $Ce_2O_3$ , 3.84 per cent. (?); didymium trioxide,  $Di_2O_3$ , and lanthanum oxide,  $La_2O_3$ , jointly 2.57 per cent.; and a profusion of the simple oxides of the commoner elements, such as iron, manganese, and silicon. So *gadolinite* has come to be regarded as one of the main sources of *yttria*, which, in its turn, yields the corresponding metal.

Following Gadolin's separation of *yttria* from *gadolinite* in 1788, Mosander further separated the earth into three parts, producing the *yttria* (as it is generally accepted to-day), *erbia*, and *terbia*. This was in 1843. Here, it seems, he abandoned his investigation, for in 1860, Berlin re-named *terbia* as *erbia*. In 1878, Delafontaine re-named the former *erbia* as *terbia*, and declared it to be incapable of further separation. Soret, in the same year, more closely investigated the newly appellation *erbia*, with the result that he separated an unknown earth (Soret's X).

Even now, these earths were not in their more elementary form. *Erbia* was further examined by Cleve (1879), and another earth, *thulia*, discovered; but this discovery settled finally the complete separation of this particular compound.

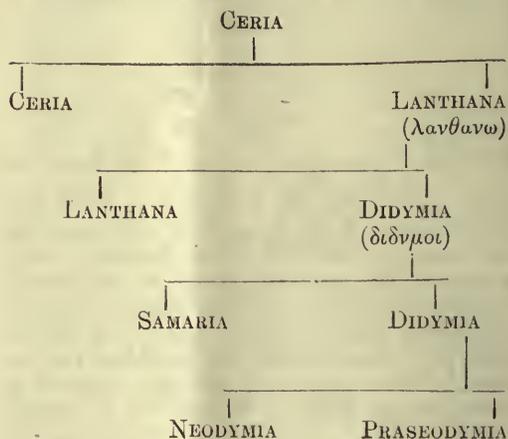
Soret's X was also studied by Cleve in the same year, and he re-named it *holmia*, although it was left to Lecoq de Boisboudran to produce yet another base, which he called *dysprosia*. In order to show the extreme complexity of the original *yttria*, the following table is appended:—



ogy is found a detailed tabulated analysis of cerite compiled from the results of Lindström (1873). The figures tally, to a certain extent, with those obtained from the recently mined specimen; but Lindström fell short of his 100 parts by 0.48 per cent. As, however, he only shows 3.44 per cent. of water, the probability is that he lost the remaining negligible percentage by evaporation. The recent specimen shows a considerable increase in water; that is to say, 5.63 per cent.

In the reduction of this earth, insoluble oxalates of the metals are precipitated from the salts in solution. Because all the earths differ from each other to such a small extent, discrimination between them, save by processes of separation and chemical peculiarities, is impossible. This branch of the subject will be dealt with later.

(d) The next of these mineral earths to be discovered was cerite. This was due to Klaproth (1803), who found it at Riddarhyttan. Subsequent examination by two other chemists was responsible for the opinion—astonishingly erroneous—that this cerite was the oxide of the new elementary metal which they christened *cerium*. Mosander, however, in 1839, proved that such was not the case, and produced another mineral which he called *lanthana*. As in the case of yttria, so in the case of ceria. This new lanthana comprised *didymia*, from which *samarium* (Boisbaudran), *neodymium* and *praseodymium* (Aver von Welsbach) were obtained. Thus a second table may be evolved, as follows:—



A specimen of cerite, mined at Löfvön, bore some similarity to Petersson's gadolinite, which was mined at Ytterby. It contained, among other compounds, 26.87 per cent. of cerium sesquioxide,  $Ce_2O_3$ ; 18.22 per cent. of didymium trioxide; and 15.95 per cent. of lanthanum oxide,  $La_2O_3$ ; the bulk of the remaining 100 parts being composed mostly of silica. In Dana's *Mineralogy* (e) *Fergusonite*, described as a niobate of erbium, cerium and yttrium, was examined by Rammelsberg. He selected a specimen from the Godthaab region in Greenland, and found that it contained 24.87 per cent. of yttrium oxide, 9.81 per cent. of erbium oxide, 2 per cent. of cerium sesquioxide, 44.55 per cent. of niobium pentoxide, 5.63 per cent. of lanthanum oxide, and 6.3 per cent. of tantalum pentoxide. In his examination, however, he fell short of the 100 parts by 0.9. There is no evidence to hand to show the cause of this deficiency, but the belief is justified that he also lost a considerable amount of water by evaporation.

A specimen obtained from Chattanooga, in Tennessee, differs widely from Rammelsberg's specimen. Here, only 20.08 per cent. of yttrium oxide was present, with a corresponding decrease in the quantities of the other oxides, and an increase in iron monoxide. Tables embodying the later analyses will be reproduced at the conclusion of this section.

(f) *Samarite*. This earth, perhaps, contains a more varied assortment of the rare earth metals than any other. It is regarded as the main source of didymia, from which the pure didymium is obtained. In 1877, Allen succeeded in analysing it with a remarkable degree of accuracy; while

Welsbach (1884-5), studying it even more closely, produced the two metals, neodymium and praseodymium. This has been already dealt with in brief, the original ceria being quoted as the primary source. Samarskite, also, contains considerable quantities of uranium and tantalum; so much, indeed, that Roscoe refers to it as "Urano-tantalate." At the same time, it is by no means the chief source of uranium, pitchblende containing the impure urano-uranic oxide,  $U_3O_8$ , to the extent of 75 per cent. approximately.

According to Allen, who obtained his specimens from the mountainous west of N. Carolina, cerium sesquioxide, didymium trioxide and lanthanum oxide are jointly present to the extent of 4.17 per cent.; while of uranium trioxide there is 12.45 per cent., and of tantalum pentoxide there is 18.2 per cent. A later specimen from the same district more or less confirms his figures. The earth is described as a tantalate and niobate of yttrium, erbium, cerium, uranium and iron.

(g) *Euxenite* has been investigated by Nilson in 1879 (*Ber. Deut. Chem. Ges.*, 1879, XII., 554), from which he obtained the oxide of scandium. Referring again to the analyses of Rammelsberg, it is composed mainly of yttrium oxide, erbium oxide, cerium sesquioxide, and the higher oxides of niobium and tin. Uranium is also present. Although Rammelsberg made a very careful separation, extending his study with great care, he failed to obtain accurate results, finally obtaining 101.59 parts. This considerable error is probably due to his estimation of niobium, the figure for which is 35.83 per cent. Proportions which will be far more acceptable are: yttrium oxide, 18.02; erbium oxide, 9.85; cerium sesquioxide, 2.38; niobium pentoxide, 32.21; stannic oxide, 25.97.

(h) *Thorite*, save for its 58.91 per cent. of thorium oxide, and its scanty complement of uranium trioxide (1.72 per cent.) is barely worth mention. *Yttrocerite*, which is the main source of cerium fluoride and yttrium fluorite, is found in numerous places, but a detailed analysis is not yet to hand; it will be dealt with more fully at a later date. *Monazite*, which was discovered by Karsten while he was investigating the properties and source of thorium, is described as a phosphate of lanthanum and cerium. Karsten gives the figures: lanthanum oxide, 23.4 per cent.; and cerium sesquioxide, 26 per cent. *Yttrotantalite* is

composed of 27.69 per cent. of yttrium oxide, 12.44 per cent. of erbium oxide, 1.9 per cent. of cerium sesquioxide, 42.12 per cent. of niobium pentoxide, and 0.22 per cent. of tungsten trioxide (Rammelsberg). *Orangeite*, investigated by Bergman, contains 74.26 per cent. of thorium dioxide. *Columbite*, investigated by Blomstrand in 1865 (*Journ. Prakt. Chem.*, 1866, XCVII., 37), varies greatly according to its locality. Whereas in Massachusetts it contains 28.55 per cent. of tantalum pentoxide and no traces of lead, the specimen obtained from Godthaab contained no tantalum whatsoever, the oxide being replaced by a considerable increase in the amount of niobium pentoxide, while the amount of lead monoxide extant is 0.12 per cent. *Tantalite* is composed, in the main, of 76.34 per cent. of tantalum pentoxide, 13.9 per cent. of iron monoxide, and 7.54 per cent. of niobium pentoxide. *Pyrochlor* contains 10.98 per cent. of titanium dioxide, 7 per cent. of cerium sesquioxide, 7.56 per cent. of thorium dioxide, and 50.11 per cent. of niobium pentoxide. Both of these last earths were investigated by Rammelsberg.

There is also an extensive list of other earths, as, for instance, *orthite*, *acanthite*, and *daleminzite*. These do not, however, yield sufficient quantities of the metals to be regarded as important. In every case, they come within the sphere of other metals, such as silver, aluminium, etc.

A few little-known rare earths are believed to exist as separate from those already mentioned. *Lanthanite* contains cerous carbonate; *decipite* is a component of some forms of samarskite; and *lanthano-tantalite* is a complex earth undiscovered until the end of 1921. These are typical examples.

(i) The accompanying table, compiled from accepted authorities, has had personal results added. The uppermost quotations are the results obtained by the chemist whose name appears at the head of the column. It would perhaps be as well to mention that the table is by no means complete, numerous unimportant oxides being omitted. It does, however, embody everything having significant bearing upon the subject in hand.

(j) Two earths have been described by various chemists as *mosandrio-* and *philippia*, but both of these have been resolved into other earths, being mechanical mixtures of the same. (*Roscoe and Schorlemmer*; II., 622).

11

TABLE SHOWING THE CHIEF COMPONENTS OF  
THE RARE EARTHS

Oxides.	Godolinite (Falkersson)	Cerite (From Dana)	Yttero- tantalite. (Rammelsberg)	Samarskite (Allen)	Euxenite. (Rammelsberg)	Monazite. (Karsten)	Fergusonite. (Rammelsberg)	Tantalite (Rammelsberg)	Thorite. (Berzelius)	Pyrochlor (Rammelsberg)
Y <sub>2</sub> O <sub>3</sub>	45.3. 48.19.	—	27.69. —	14.48. 12.97.	17.23. 18.02.	—	24.87. 20.08.	—	—	—
Ce <sub>2</sub> O <sub>3</sub>	3.84# 1.07	24.06 26.87.	1.9 —	4.17# 2.05.	2.34. 2.38.	26.0 —	2.0 1.67	—	—	7.0. —
Di <sub>2</sub> O <sub>3</sub>	2.57* 2.3	35.37. 18.22.	—	0.08	—	—	—	—	—	—
La <sub>2</sub> O <sub>3</sub>	0.08.	15.95.	—	2.61	—	23.4 —	5.63 5.0	—	—	—
Er <sub>2</sub> O <sub>3</sub>	—	—	12.44 —	—	9.39 —	—	9.81 —	—	—	—
ThO <sub>2</sub>	0.41 0.12	—	—	—	—	17.95 —	—	—	58.91 56.32	7.56 —
Ta <sub>2</sub> O <sub>5</sub>	—	—	10.05 —	18.2 18.22	—	—	6.3 4.93	76.34 —	—	—
TiO <sub>2</sub>	—	—	—	—	—	—	—	—	—	10.47 —
UO <sub>2</sub>	—	—	1.26 —	—	8.86 9.31.	—	2.58 2.82	—	—	—
UO <sub>3</sub>	—	—	—	12.54 11.31.	—	—	—	—	1.64 0.95	—
WO <sub>3</sub>	—	—	0.22 —	0.08* 0.13*	—	—	0.15 0.25	—	—	—
FeO	12.89 11.25	3.92 2.03	0.63 —	10.75 12.6	3.61 3.09	—	0.74 4.66	13.9 —	—	1.84 —
Fe <sub>2</sub> O <sub>3</sub>	0.6 0.94	— 2.71	—	—	—	—	—	—	3.46 6.88	—
CaO	0.54 1.2	4.35 4.3	2.31 —	0.55 0.48	—	1.68 —	0.61 0.58	—	—	14.21 —
ZrO <sub>2</sub>	—	—	—	0.1	—	—	0.03	—	—	—
Nb <sub>2</sub> O <sub>5</sub>	—	—	42.12 —	37.5 38.61	35.83# 32.21	—	44.45 40.35	7.54 —	—	53.19 —
of Lead	— 0.13	—	—	—	—	—	—	—	0.82 1.3	—
of Tin	—	—	0.24 —	—	24.33 25.97	2.1 —	0.47 —	0.7 —	0.01 —	—
of Aluminium	—	1.26 0.88	—	—	—	—	—	—	0.06 0.09.	—
of Potassium	—	— 0.02	—	—	—	—	—	—	0.15 0.14	—

\* Conjointly with La<sub>2</sub>O<sub>3</sub>.

\* WO<sub>2</sub> in these instances.

# Conjointly with Di<sub>2</sub>O<sub>3</sub> and Ce<sub>2</sub>O<sub>3</sub>.

A considerable number of the more elementary earths have been formulated. *Keilhauite*, for instance, has been symbolised thus: Ca Y (Ti Al Fe) SiO<sub>5</sub>. A vanadium-bearing earth, *vanadinite* (also described as lead vandate, in spite of the presence of a chloride) has the formula: 3Pb<sub>3</sub> (VO<sub>4</sub>)<sub>2</sub> + PbCl<sub>2</sub>, also Pb<sub>3</sub> (VO<sub>4</sub>)<sub>2</sub> + Pb<sub>2</sub> (VO<sub>4</sub>) Cl. For most practical purposes of expression, the method is sound enough, as it denotes the main components of the earths. It does not admit the embodiment of their natural composition, however, consequently is far from accurate. It is also cumbersome. Let the composition of samarskite be considered as a case in point. This is determined to be a nioba-tantalate of thirteen rare earth metals, calcium, uranium and iron. To express this as a formula would be absurd, and its very complexity, by virtue of the number of symbols, would tend to confound.

## APPARATUS FOR THE RECOVERY OF BROMINE FROM SODIUM HYPOBROMITE.

By C. H. COLLINGS.

### I.—THE APPARATUS.

In *The Chemical News* for December 1, 1916, I described a simple apparatus to recover bromine from sodium hypobromite, whether new or stale, used or not, and to at once recombine it with NaHO as fresh hypobromite. The method was simple: to mix slowly the waste hypobromite with a mineral acid, thus gradually disengaging the Br, simultaneously aspirating the latter as a vapour into fresh NaHO. In its first form, the apparatus suffered from one marked defect, however, and that was the considerable residuum of Br left in the mixed acid and waste. A fair amount of experimenting was needed to overcome this; but the improved form now illustrated has been in use for a considerable time with consistently satisfactory results, and I would call the attention of all considerable users of sodium hypobromite to it as a simple, compact, effective and rapid means of recovering Br from waste that otherwise goes down the sink, to the distinct disadvantage of their pockets. The new form does not require skilled attention, and practically speaking, runs itself; further, no Br vapour can escape into the air of the room. By its use one can even avoid altogether the need to handle and store Br

as such, as by obtaining the hypobromite ready-made one can readily recover from it needed Br (to recombine as NaBrO) as convenient. This creates a great advantage, by eliminating the cost, delay and trouble attending the transit of a dangerous chemical like Br; further, where admission of Br into one's geographical area happens to be inhibited, the hypobromite may be imported and regarded, from the point of view of the apparatus, as a convenient storehouse of Br.

On reference to the illustration (kindly lent by Messrs. Baird and Tatlock, who are putting the apparatus on the market), it will be seen that the operations needed are few and simple. The whole thing is connected up first with an aspirator or pump at (P). Caustic soda solution of the usual hypobromite formula is introduced into (HJ) via the calibrated cup (H). Acid (HNO<sub>3</sub>) is poured into (A) up to the mark, then run into the mixing-chamber (MC), and the acid tap turned off. Waste hypobromite from which the Br is to be extracted is poured into (W) up to the mark, the aspirator started, the tap of (W) timed to allow a drip of 60 or fewer drops to the minute—and the affair may be left to run itself with, perhaps, one subsequent readjustment, if necessary, of the dripping tap. The stream of aspirated air passing through the reacting substances from bottom to top, carries practically the whole of the Br, by degrees, into the waiting NaHO and so forms new hypobromite. The valve (V) is nearly filled with NaHO solution (not water), and both physically and chemically inhibits any back pressure of Br into the air of the room. The whole process takes about 20 minutes. The mixed acid and exhausted waste are then emptied (by turning the tap at bottom of mixing-chamber) into (RJ) below.

### II.—ON CERTAIN EXPERIMENTS WITH THE APPARATUS.

Having established the successful working of the apparatus, and observed that (as might be expected) a slight residuum of unrecoverable Br remained behind, in solution, in the mixing-chamber, the next step was to ascertain the allowance to be made for this in fixing the quantity of waste sodium hypobromite from which 2.2 cc. of Br could be actually recovered to recombine with fresh NaHO solution in the hypobromite jar. The simplest way was to exhaust the urea-decomposing power of ordinary hypobromite, made according to

the usual formula (25 cc. NaHO + 2.2 cc. Br), recover the Br from this, similarly exhaust the recovered Br hypobromite, and compare the total N percentages in each case (expressed as urea): thus obtaining the ratio by which the extra quantity of waste sodium hypobromite to anticipate Br loss in the mixing-chamber could be directly calculated. This necessary experiment led to a quite unexpected result.

The total urea percentage obtained by exhausting ordinary hypobromite was found to range around 9.5. Such exhausted hypobromite then yielded up its Br *via* the apparatus into a new lot of NaHO, and the corresponding figure of *this*, so far from being less than 9.5, was found (in each of several experiments) to range round 11.3 per cent.! Again, such an exhausted hypobromite was instead kept for a week, its Br recovered, recombined as hypobromite, and duly exhausted. It gave a total of 11.8 per cent. of urea.

It is a familiar fact that sodium hypobromite has to be newly made for urea estimation, as it soon deteriorates as regards this function. I have found the rate of deterioration to be about 10 per cent. per day, the percentage not being calculated on the initial value, after the first day, but on the residual value of each day. Now the singular thing is that, as far as my experimenting has gone, hypobromite that has been kept a week in its original unused condition (and whose urea value in the first instance would be about 9.5) on being passed through the apparatus yielded Br that, combined with the usual 25 cc. NaHO, produced a hypobromite of total urea value of 13.3 per cent. Further, hypobromite made in the usual way, and similarly treated without waiting a week, produced hypobromite of total urea value of 13.0 per cent.

The practical consequence of these figures is that an amount of waste equal to the contents of the original hypobromite bottle is quite adequate to yielding a sufficiency of Br, which, recombined under the conditions ruling in the apparatus, more than balances the trifling loss of Br in the mixing-chamber. This holds good whether the original hypobromite be newly made and used or not, or has stood a week unused, or has been used new and is now stale, or used when stale, and is either partially or wholly exhausted.

The above facts and figures suggest more than one problem of varying interest.

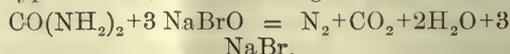
Two of them might be briefly considered:

(1) The total urea-decomposition capacity of recovered Br, when recombined with NaHO, is, in the first recovery, greater than that of the hypobromite from which it has been recovered.

(2) Such increase is greatest in the case of unused hypobromite, new or even ten days old.

Regarding (1)—

When urea is "acted upon" by sodium hypobromite, the following ensues:—



This reaction may be the outcome of simple chemical affinity (as is implied by the expression "acted upon") between the urea and the NaBrO: although as no combination of any kind between the urea or any of its constituents is formed with NaBrO or NaBr, chemical affinity would seem hardly a happy term. Further, as NaBrO spontaneously breaks down into NaBr and O, it can hardly be called reduction. Alternatively, in view of the fact that from its first formation NaBrO steadily breaks down into NaBr and O, it may be that urea exerts a catalytic action on it, accelerating its transformation from NaBrO to NaBr. The rapid disengagement of O atoms at once ensuing would react upon the urea, to each molecule of which three atoms of O, as per the equation, would be attracted, leading to its breaking down into free N, CO<sub>2</sub> and H<sub>2</sub>O. This explanation seems, on the face of it, to be as good as the other, and for this reason the catalytic hypothesis, if not already entertained, might be considered.

We are now, however, concerned with the composition of the mixture usually, in urine analysis, referred to as sodium hypobromite. The nature of this demands close scrutiny if we are to cope with the two points just raised, and explain in a rational manner the associated percentage figures. The usual equation is:—  
 $\text{Br}_2 + 2\text{NaHO} = \text{NaBr} + \text{NaBrO} + \text{H}_2\text{O}.$   
 Here the ratio of Br-O to total Br is as 2 to 4.

It will be borne in mind, of course, that the NaBrO at once, slowly and steadily spontaneously parts with its oxygen and becomes the stable but useless form, NaBr. Hence sodium hypobromite does not "keep."

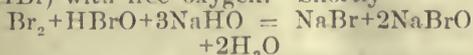
Now, to explain the increased power of the hypobromite solution, as furnished by



the apparatus, we must keep in mind at least three points: that the urea breaks down in response to the action of oxygen atoms qualified by their intimate association with Br atoms up to the last moment; that, consequently, oxygen linked with Br must be present to the maximum extent; that sources of oxygen other than those available under ordinary circumstances, be demonstrated. The Br is, for practical purposes, a constant factor.

In the case of sodium "hypobromite" made in the usual way for urine analysis, there is practically always a slight white precipitate. This is evidently  $\text{NaBrO}_3$ , formed as a consequence of the heat evolved, and represents so much unavailable oxygen (+ Br, in solid form) for the purposes of urea decomposition. The usual solution, then, starts handicapped. In hypobromite made in the apparatus there is no such precipitate, doubtless owing to the cooling effect of the rapidly passing air bubbles through the forming hypobromite—which latter, again, forms relatively slowly, thus keeping down the temperature and avoiding the precipitation of  $\text{NaBrO}_3$ : hence, in the apparatus-formed hypobromite, a trifle extra  $\text{NaBrO}$  is derived from this circumstance.

During the mixing process between the acid and the waste sodium hypobromite, with the evolution of free Br, passes from the bottom of the chamber up through the mixed acid and waste, the purpose of which is to disengage from the mixture the Br freed by the acid, and to carry it, together with that in the air of the mixing-chamber, in vapour form to the bottle in which NaHO awaits it to form therewith fresh hypobromite. It seems possible that besides doing this, the air may contribute a little of its oxygen to the general atomic rearrangement going on, which, with easily available hydrogen would combine with a modicum of the Br into hypobromous acid. The latter, in aqueous solution, passes over in vapour form, to be decomposed in the NaHO bottle, and so forcibly contribute an extra atom of oxygen along with its atom of Br: the first stage of this process being perhaps reduction to hydrobromic acid (HBr) with free oxygen. Shortly—



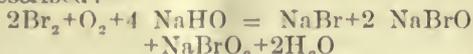
(Ratio of BrO to total Br, 2 to 3).

White fumes of what almost certainly would be hydrobromic acid have been observed on different occasions at the top of

the mixing-chamber and simultaneously in the delivery-tube, NaHO bottle and even, rarely, as far as the aspirator itself.

So far the above two equations correspond roughly to the figures obtained with hypobromite made in the usual way (9.5 circa) and those from recovered exhausted hypobromite (11.5 circa) with ratios of 0 to Br as 2 to 4 and 2 to 3 respectively, i.e., an increase of urea-detonating oxygen in the latter case over the former. There still remain the figures (13.0 circa) obtained from hypobromite made from Br recovered from hypobromite, new or stale, that has remained unused. Now, as the  $\text{NaBrO}$  steadily breaks down to  $\text{NaBr}$  and free O it seems reasonable to assume that such unused hypobromite contains spare oxygen either still in temporary combination with  $\text{NaBr}$  or but lately parted therefrom. This would go to enrich the oxygen content of the air stream, and would thus bring into contact with the nascent Br vapour an atmosphere especially full of oxygen: circumstances peculiarly favourable to the formation of fully oxidised Br compounds. Here, then, I would suggest an hypothesis, not (I think) altogether unreasonable, and one moreover that assists to meet and explain the observed facts, viz., that a compound usually assumed not to exist may be formed under these unusual circumstances, to wit, sodium bromite ( $\text{NaBrO}_2$ ): a compound which at the cost of merely the usual one, necessary, Br atom, would furnish double the reaction energy ( $\text{O}_2$ ) in relation to its dissociating action upon the urea molecule.

Assuming this for the moment, and excluding *pro temp.* the hypothesis of  $\text{HBrO}$  being formed and carried over, let us write an equation corresponding to the possible facts: no more than one free oxygen molecule being added to represent the contribution of the rich atmosphere previously described:—



With a ratio of BrO to Br as 2 to 2.

I do not know if this view will be accepted; but this can at least be said for it, that it furnishes the necessary mechanism to account for the observed result, for the startling increase (approaching 40 per cent.) in the total urea decomposable by hypobromite made in this manner (in the apparatus) over that made in the usual way, Br and NaHO being as near as may be identical quantities in each case—the

Br, if anything, being a trifle less in the recovered quantity. Equally, has sodium hypobromite been put together in this manner by other experimenters, the Br largely as vapour with a copious admixture of, at least atmospheric oxygen? If not, it might be worth someone's while to do it, and see what may happen under these conditions.

## PROCEEDINGS AND NOTICES OF SOCIETIES.

### THE ROYAL SOCIETY.

#### LIST OF PROBABLE PAPERS FOR READING, JANUARY 25, 1923.

PROF. A. V. HILL, F.R.S., *The Potential Difference occurring in a Donnan Equilibrium and the Theory of Colloidal Behaviour.*

E. F. ARMSTRONG, F.R.S., and T. P. HILDITCH, *A Study of Catalytic Actions at Solid Surfaces. X.—The Interaction of Carbon Monoxide and Hydrogen as conditioned by nickel at relatively low Temperatures. A Practical Synthesis of Methane.*

J. HOLKER, D.Sc., *The Periodic Opacity of certain Colloids in progressively increasing Concentrations of Electrolytes.* Communicated by Prof. A. V. Hill, F.R.S.

E. K. RIDEAL and R. G. W. NORRISII, *The Photochemistry of Potassium Permanganate. Part I.—The Application of the Potentiometer to the Study of Photochemical Change. Part II.—On the Energetics of the Photo-decomposition of Potassium Permanganate.* Communicated by Sir William Pope, F.R.S.

E. A. FISHER, *Some Moisture Relations of Colloids. I.—A Comparative Study of the Rates of Evaporation of Water from Wool, Sand and Clay.* Communicated by Prof. A. Smithells, F.R.S.

R. WHYTLAW-GRAY, J. B. SPEAKMAN, and J. H. P. CAMPBELL, *Smokes, A Study of their Behaviour and a Method of Determining the Number of Particles they contain.* Communicated by Prof. A. Smithells, F.R.S.

R. WHYTLAW-GRAY and J. B. SPEAKMAN, *A Method of determining the Size of the Particles in Smokes. Part II.* Communicated by Prof. A. Smithells, F.R.S.

R. C. DAY, *The Effect of long Grinding on Quartz (Silver Sand).* Communicated by Dr. M. W. Travers, F.R.S.

THURSDAY, JANUARY 18, 1923, AT 4.30 P.M.

Papers read:—

J. BARCROFT, F.R.S., *Observations on the Effect of High Altitude on the Physiological Processes of the Human Body.*

PROF. E. W. MACBRIDE, F.R.S., *Remarks on the Inheritance of Acquired Characters.* (Verbal communication only).

C. F. COOPER, *Baluchitherium osborni.* (? syn. *Indricotherium turgaicum.* Borrisyak). Communicated by Dr. A. S. Woodward, F.R.S.

J. A. GUNN and K. J. FRANKLIN, *The Sympathetic Innervation of the Vagina.* Communicated by Sir Charles Sherrington, P.R.S.

H. G. CANNON, *On the Metabolic Gradient of the Frog's Egg.* Communicated by Prof. E. W. MacBride, F.R.S.

BASISWAR SEN., *On the Relation between Permeability Variation and Plant Movements.* Communicated by Sir William Bayliss, F.R.S.

H. L. DUKE, M.D., *An Enquiry into an Outbreak of Human Trypanosomiasis in a "Glossina morsitans" Belt to the East of Mwanza, Tanganyika Territory.* Communicated by Mr. C. Dobell, F.R.S.

LOUIS DOLLO, Sc.D., *Le Centenaire des Iguanodons (1822-1922).* Communicated by Prof. A. C. Seward, F.R.S.

### MINERALOGICAL SOCIETY.

JANUARY 9.

Dr. A. E. H. Tutton, Past-President, in the chair.

A. BRAMMALL and H. F. HARWOOD, *Dartmoor occurrences of (1) rutile, brookite and anatase, (2) zircon.*

(1) Anatase, with less abundant brookite and scanty rutile, is common in Dartmoor stream-sands, etc. Anatase and brookite, absent from the unaltered grey granite, have been found in pneumatolysed rocks, especially "red" granites, and the mode of genesis of these two minerals is discussed. Data provided by chemical work on "baueritised" Dartmoor biotite (containing about 1.8 per cent. TiO<sub>2</sub>) and by the occurrence of anatase granules encrusting detrital grains of ilmenite are examined in their bearing on the possibility that some anatase may have developed (or existing crystals may have continued to grow) in detrital material after sedimentation.

(2) Two strongly contrasted kinds of zircon crystals are described: differences in crystal habit, nature of inclusions, and mode of occurrence in the granite suggest that the dominant kind, which is tawny, zoned, and rich in inclusions, crystallised out from the magma early, and that the subordinate kind, water-clear and containing few inclusions, separated out at a much later stage.

DR. L. J. SPERCER, with chemical analyses by E. D. MOUNTAIN, and microscopical determinations of the pseudomorphs by W. CAMPBELL SMITH, *A davyne-like mineral and its pseudomorphs from St. John's Island, Egypt.*

Two small crystals found with peridot, garnierite, etc., showed the physical characters of davyne, but consist of a complex silicate (with sulphate and carbonate) of aluminium, calcium, magnesium, and sodium, together with a considerable amount of water. Pseudomorphs after this material are more abundant: they consist of a complex of hydrated silicates of aluminium and magnesium, together with small amounts of corundum and spinel.

UNIVERSITY OF LONDON, KING'S COLLEGE, AND KING'S COLLEGE FOR WOMEN.

PUBLIC LECTURES AND ARRANGEMENTS IN THE LENT TERM, 1923.

Admission to public lectures is free and without ticket unless otherwise stated. When cards of admission are required, they can be obtained on application to the Registrar, to whom all enquiries with regard to public lectures should be made in the first instance. A stamped addressed envelope should be enclosed.

FACULTY OF NATURAL SCIENCE.

*A Course of Eight Public Lectures, on Wednesdays, at 5.30 p.m.*

"SOME ASPECTS OF NATURAL PHILOSOPHY."

January 24: "The Quest of Science Today, and as exemplified in its History," by Professor A. N. Whitehead, F.R.S., M.A., Sc.D. (Camb.), LL.D. (St. Andrews), D.Sc. (Manchester).

January 31: "The Measurement of Stellar Distances," by The Astronomer Royal.

February 7: "The Fundamental Conceptions of Biology," by Dr. J. S. Haldane,

F.R.S., M.A., M.D., LL.D. (Edin.), M.A. (Oxford), LL.D. (Birmingham).

February 14: "The Succession of Floras in the Past," by Dr. Dukinfield Scott, F.R.S., M.A., LL.D., D.Sc.

February 21: "A Physico-Chemical Theory of the Instability of Western Civilisation," by Professor F. Soddy, F.R.S., M.A.

February 28: "The Limitations of Natural Science," by Principal L. P. Jacks, C.A. (Lond.), Hon. M.A. (Oxford), Hon. LL.D. (Glasgow), Hon. D.Litt. (Liverpool), Hon. D.D. (Harvard).

March 7: "Some Thoughts on the Relations of Science and Industry," by Sir Herbert Jackson, K.B.E., F.R.S., A.R.C.M., F.I.C., F.C.S., Director of Research, British Scientific Instruments Research Association; Emeritus Professor of Chemistry, University of London.

March 14: "The Influence of Science," by Sir Richard A. Gregory, D.Sc. (Leeds), F.R.A.S., F.Inst.P., F.J.I.

DEPARTMENT OF CLASSICS AND HISTORY.

An inaugural lecture will be delivered on Friday, January 19, at 5.30 p.m.,

"PROLEGOMENA TO THE STUDY OF ANCIENT GREECE,"

by Edwyn Bevan, M.A., LL.D., Lecturer in Hellenistic Language and Literature.

FACULTY OF THEOLOGY.

*A Course of Three Public Lectures (arranged by the University), at 5 p.m., on March 8, March 13, and March 15.*

"ETHICS AND THE PHILOSOPHY OF HISTORY,"

by Professor Ernst Troeltsch, of the University of Berlin.

*A Course of Ten Public Lectures, on Tuesdays, at 5.30 p.m., illustrated by Lantern Slides.*

"SIXTEENTH-CENTURY ART."

Commencing January 23.

Tickets for these lectures can be obtained before each lecture outside the Great Hall, or between 10 and 4 at the College Office. Fee: 1s. for one lecture, 7s. 6d. for the course of ten. By the Rev. Percy Dearmer, D.D., Professor of Ecclesiastical Art.

*A Course of Six Public Lectures and Practices, on Mondays, at 5.30 p.m.*

"ECCLESIASTICAL MUSIC."

Commencing February 5.

This course is arranged by the Rev. C. F. Rogers, M.A., Professor of Pastoral Theology.

## DEPARTMENT OF HISTORY.

*A Course of Six Public Lectures (arranged by the University), on Thursdays, at 5.30 p.m., beginning January 18.*

## "THE NOMADS OF CENTRAL ASIA."

By Professor V. Barthold, Professor of the University of Petrograd.

## DEPARTMENT OF PHILOSOPHY.

*A Course of Six Public Lectures, on Tuesdays, at 5.30 p.m., commencing February 20.*

## "PHYSICAL CASUALTY AND MODERN SCIENCE."

By H. Wildon Carr, D.Litt., Professor of Philosophy.

*A Course of Four Public Lectures on Tuesdays, at 5.30 p.m., commencing January 23.*

## "THE ENIGMA OF SOCRATES."

By Miss Hilda D. Oakeley, M.A., Reader in Philosophy.

*A Course of Three Public Lectures on Fridays, at 5.30 p.m., commencing March 2.*

## "THE CASE FOR PLURALISM."

By C. E. M. Joad, M.A.

## DEPARTMENT OF PSYCHOLOGY.

*A Course of Three Public Lectures on Mondays, at 5.30 p.m., commencing February 19.*

## "PSYCHOLOGY AND PSYCHOTHERAPY."

By William Brown, M.A., M.D., D.Sc., M.R.C.P., Wilde Reader in Mental Philosophy in the University of Oxford, and Honorary Consulting Psychologist, Bethlem Royal Hospital, etc.

## SCHOOL OF SLAVONIC STUDIES.

The following lectures will be delivered in Room 14D, unless otherwise stated:

*A Course of Eight Public Lectures on "POLAND,"*

*On Mondays, at 5.30 p.m., commencing January 22.*

By Professor Roman Dyboski (Professor of English Literature in the University of Cracow).

*A Public Lecture, on Monday, February 5, at 5.30 p.m.*

## "THE ORIGINAL HOME OF THE SLAVS."

By N. B. Jopson, M.A., Reader in Comparative Slavonic Philology.

*A Course of Nine Public Lectures, on Tuesdays, at 5.30 p.m., commencing January 23.*

## "CONTEMPORARY RUSSIA FROM 1861."

By Sir Bernard Pares, K.B.E., Professor of Russian.

*A Course of Three Public Lectures, on Thursdays, at 5.30 p.m., beginning January 25.*

## "MODERN CZECH NOVELISTS."

By Otakar Voadlo, Doctor of the University of Prague; Lecturer in Czechoslovak.

*Two Public Lectures, on Thursdays, at 5.30 p.m.*

February 15: "Slowacki and the King Spirit."

February 22: "Some Poetry of Mickiewicz."

By Leonard Wharton, M.A., Lecturer in Polish Literature.

*A Public Lecture, on Thursday, March 1, at 5.30 p.m.*

## "POST-WAR POETRY IN POLAND."

By F. Sobienowski.

*Three Public Lectures, on Thursdays, March 8, 15, and 22, at 5.30 p.m.*

"THREE RUSSIAN POETS, PUSHKIN, LESKOV, AND BLOK."

By Prince D. S. Mirsky, Lecturer in Russian Literature.

*A Course of Ten Public Lectures, on Fridays, at 5.30 p.m., commencing January 19.*

## "SERBIA AND THE JUGO-SLAV MOVEMENT."

By R. W. Seton-Watson, D.Litt., Professor of East European History.

## SCHOOL OF SPANISH STUDIES.

*A Course of Three Public Lectures, on Thursdays, February 22, March 1, and March 8, at 5.30 p.m.*

## "THE PRESENT CONDITIONS, HISTORIC ORIGINS AND RECENT REFORMS OF SPANISH EDUCATION."

By Senor Don José Castillejo, Professor in the University of Madrid and Secretary to the Junta para Ampliacion de Estudios.

H.E. The Spanish Ambassador will take the chair at the first lecture.

Those particularly interested in this course should enquire from the Registrar (enclosing a stamped addressed envelope).

*Two Public Lectures, on Thursday, March 15, and Thursday, March 22, at 5.30 p.m.*

## "THE TENDENCIES OF THE SPANISH DRAMA SINCE 1868."

By Walter Fitzwilliam Starkie, M.A., Trinity College, Dublin.

## DEPARTMENT OF MODERN GREEK

*A Course of Six Public Lectures, on Tuesdays, at 5.30 p.m., commencing February 20.*

## "THE EXPANSION OF EUROPE OVERLAND: THE ROUTE OF THE STEPPES."

The first of these lectures will be illustrated by lantern slides.

By A. J. Toynbee, M.A., Professor of Modern Greek.

DEPARTMENT OF ZOOLOGY.

*A Course of Three Public Lectures (arranged by the University), on February 20, 22, and 23, at 5.15 p.m.*

"THE BIONOMICS OF MARINE ANIMALS."

By J. H. Orton, D.Sc.

FACULTY OF LAWS.

*A Public Lecture (arranged by the University), on Friday, February 9, at 5.30 p.m.*

"CHIEF JUSTICE SIR WILLIAM BEREFOED."

By W. C. Bolland, M.A., Sanders Reader in Bibliography at the University of Cambridge.

DEPARTMENT OF ENGINEERING.

*Three Courses of Advanced Lectures for Post-Graduate and other Advanced Students.*

1. "Recent Developments in Electrical Traction." Three lectures by F. Lydall, B.A., B.Sc., M.I.E.E., on Tuesdays, at 5.30 p.m., beginning January 23.

2. "Recent Developments in Central Station Design." Three lectures by W. B. Woodhouse, M.Inst.C.E., M.Inst.E.E., on Mondays, at 5.30 p.m., beginning February 12.

3. "The Erection of Steelwork." Three lectures by J. Stuart Lewis, on Tuesdays, at 5.30 p.m., beginning March 6.

These lectures are free only to engineering students of the College.

SHAKESPEARE ASSOCIATION.

Friday, January 26, 5.30 p.m.: Professor Parrott, of Princeton University, "Tmon of Athens."

Friday, February 16, 5.30 p.m.: Dr. Scripture, "Shakespeare's Verse in the Light of Experimental Phonetics." (With lantern illustrations.)

Friday, March 16, 5.30 p.m.: Bibliographical Meeting.

OTHER ARRANGEMENTS.

Wednesday, January 17: College Term begins. 10 a.m. Service in the College Chapel.

Thursday, January 18: University Term begins.

Monday, January 22, 6 p.m.: Gilbert Lectures on Banking, first of a course of four lectures by Mr. Heber Hart, K.C.

Thursday, March 15, 6 p.m.: Gilbert Examination.

Wednesday, March 28: College and University Terms end.

ERNEST BARKER, M.A., D.LITT., LL.D.,  
Principal.

W. R. MATTHEWS, M.A., D.D., Dean.

S. T. SHOVELTON, M.A., Secretary.

UNIVERSITY OF BIRMINGHAM.

Principal Grant Robertson, of the University of Birmingham, states, in his annual report, that the Standing Joint Committee of Council and Senate "to organise a policy of research" has been in full working for the whole session. The appointment of the Committee was a wise step, excellent work having already been done. It is clear that the existence of such a Committee has stimulated the impetus towards research, and that the number of applications from the staff will increase. It is, above all, important that research (he says) should not be identified solely with work carried on by the Faculty of Science, essential as that is, but that every Faculty should realise that original contributions to knowledge are a duty, which is closely connected with efficiency in teaching, and that the influence thereby exercised on the students is incalculable alike in its value and in the attitude of mind it can create.

CUPROUS SULPHITES.

It was suggested in a previous communication, published in *The Chemical News* of March 4, 1921, that the yellow cuprous oxide, obtained by an alkaline solution of cupric sulphate with glucose, might contain an appreciable amount of cuprous hydroxide. Attempts were made to prepare cuprous salts of some oxygen acids with this yellow oxide. In the course of these trials a red variety of basic cuprous sulphite was detected. Its method of preparation and properties are detailed below.

KNOWN SULPHITES.

Besides the white cuprous sulphite, obtained by passing sulphur dioxide through a solution of cuprous acetate in acetic acid, a garnet-red cupro-cupric salt (Sp. Gr. 3.57)— $\text{Cu}_2\text{SO}_3 \cdot \text{CuSO}_3 \cdot 2\text{H}_2\text{O}$ —is

known to exist. It is prepared by heating the double salt, cuprous ammonium sulphite. Another cupro-cupric salt— $\text{Cu}_2\text{SO}_3$ ,  $\text{CuSO}_3 \cdot 5\text{H}_2\text{O}$ —greenish yellow in colour, is also mentioned.

#### PREPARATION.

Basic cuprous sulphite can be prepared by saturating, with sulphur dioxide, a weak solution of sodium or potassium hydroxide in which yellow cuprous oxide is suspended. A bright red, heavy (Sp. Gr. 3.26) granular precipitate settles down in a few minutes. The substance so prepared was washed free from sulphites and other impurities, dried at  $105^\circ\text{C}$ ., and used in the following experiments.

#### PROPERTIES.

1. When heated in a test tube, the substance loses  $\text{SO}_2$  and  $\text{H}_2\text{O}$ , the residue becoming yellow, then red, and finally black. When gradually heated in the air-oven, it undergoes no change up to  $145^\circ\text{C}$ ., when it begins to lose water. The residue—greyish yellow in colour—contains cupric sulphate and bright yellow cuprous oxide.

2. When boiled with water, a small portion of the salt is readily hydrolysed, and a bright lemon yellow substance sticks fast to the bottom of the vessel as a thin layer. It readily dissolves in caustic alkalis, forming a pale blue solution. The rest of the substance slowly hydrolyses with the formation of cupric sulphate and yellow cuprous oxide.

3. With dilute hydrochloric acid cuprous chloride is formed with the evolution of sulphur dioxide.

4. With dilute alkalis a pale blue solution containing alkali sulphite is formed and yellow cuprous oxide is deposited with no trace of cupric hydroxide. When the blue solution is warmed, yellow cuprous oxide is thrown out, and pure alkali sulphite remains in solution.

5. The substance is not affected by sulphurous acid.

#### COMPOSITION.

To ascertain the composition of the substance several determinations were made which gave consistent results with the following percentages:—

	%
(a) Cu—estimated as $\text{CuO}$ .....	50.46
(b) $\text{SO}_3$ —estimated as $\text{SO}_2$ by ... treating the salt with dilute HCl and absorbing the $\text{SO}_2$ in NaOH .....	21.15
(c) $\text{H}_2\text{O}$ —calculated from loss of weight on heating the salt in air oven up to $160^\circ\text{C}$ . .....	4.65

(d) The substance, after heating in the air oven up to  $160^\circ\text{C}$ . was treated with water; the resulting yellow cuprous oxide was washed free from  $\text{CuSO}_4$ , dried and reduced to metallic copper in a current of hydrogen. The percentage of copper was found to be 59.12, giving the formula  $\text{Cu}_2\text{O} \cdot 4\text{H}_2\text{O}$  to the yellow oxide. Hence the  $\text{H}_2\text{O}$  and  $\text{O}_2$  which are in combination with copper as this hydrated yellow oxide must account for the remaining 23.74 per cent. of the salt required to complete the percentage composition of the substance ( $100 - 76.26$ ) ..... 23.74

These percentages do not accord with the composition of either of the cupro-cupric salts mentioned above. The general behaviour and percentage composition, as given above, point to the conclusion that the red substance under investigation is a basic cuprous sulphite and cannot be identified with either of the cupro-cupric sulphites which are known to exist. Its formula—which accords with its percentage composition—may probably be  $\text{Cu}(\text{Cu}_2\text{O} \cdot 4\text{H}_2\text{O})\text{SO}_3 \cdot \text{H}_2\text{O}$ , in which a molecule of hydrated yellow cuprous oxide takes the place of one hydrogen atom in sulphurous acid while the other hydrogen atom is displaced by monovalent copper.

V. V. SARMA.

*Govt. College Laboratory,  
Kumbakonain, S. India.  
20th December, 1922.*

#### GENERAL NOTES.

#### PREPARATION OF A TRIOXYMETHYLENE.

By D. L. HAMMICK AND A. R. BOERCE.

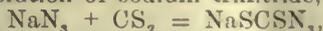
a Trioxymethylene is a polymeride of formaldehyde, and can be prepared by a modified form of Pratesi's method, which consists in heating 10 parts of paraformaldehyde and one part of 1:1 sulphuric acid in a vacuum tube to  $115^\circ\text{C}$ . in an oil bath. The crystalline trioxymethylene forms as slender needles on the cool part of the tube. The yield of purified substance is 10 per cent. Better results were obtained on the

lines of Anerbach and Barschall's process under definite conditions. By repeated sublimation of a trioxymethylene, a new polymeride,  $\epsilon$  polyoxymethylene, is formed.—(*Trans. Chem. Soc.*, 1922, p. 2738.)

#### ABSORPTION OF CARBON DISULPHIDE VAPOUR.

By A. J. CURRIER AND A. W. BROWNE.

For the absorption of carbon disulphide vapour from gases, the authors propose to use a solution of sodium trinitride,



in which the trinitride and carbon disulphide combine to give sodium azido-dithiocarbonate. The strength of the sodium trinitride solution should be at least 5 per cent., and although aqueous solutions of sodium azido-dithiocarbonate decompose to give free nitrogen gas, this decomposition is too slow to affect the results in gas analysis.—(*J. Am. Chem. Soc.*, 1922, p. 2849.)

#### BOARD OF TRADE ANNOUNCEMENT. DYESTUFFS ADVISORY LICENSING COMMITTEE.

The Board of Trade announce that on the nomination of the Association of British Chemical Manufacturers, they have appointed Mr. W. H. Dawson, the Manager of the British Alizarine Company, Limited, Trafford Park, Manchester, to be a member of the Dyestuffs Advisory Licensing Committee, set up under Section 2 (3) of the Dyestuffs (Import Regulation) Act, 1920, in the place of Mr. E. V. Evans, O.B.E., F.I.C., resigned; and that they have appointed Mr. Lionel Blundell, of the North British Chemical Co., Ltd., Droylesden, Manchester, to be a member of the Dyestuffs Industry Development Committee, set up under Sub-Section 2 (6) of the Dyestuffs (Import Regulation) Act, 1920, in the place of Mr. E. V. Evans, O.B.E., F.I.C., resigned.

*Board of Trade, 10th January, 1923.*

#### PERU.

##### A LAND OF MYSTERY.

Peru, in which once flourished the ancient civilisation and culture of the Incas, is still a land of mystery. Though not large as South American Republics are measured, it is three countries with three

distinct climates. The tropical lowlands of the steaming Amazon valley are cut off from the temperate coast region of the Pacific by mountain ranges within which dwell Indians in a low state of civilisation and in a chronic condition of unrest. The dry coast strip, cooled by the Humboldt current, contains the principal cities and most of the white population of some 700,000 people. There is here little or no rainfall, the land is cultivated by irrigation, and the products are cotton and sugar, wool, hides and skins, and petroleum. This coastal strip, though limited in area, is the chief district in which agriculture and pasture flourish. The rain, which is denied to the coastal region by the barrier of the Andes, falls abundantly all the year round in the mountain districts. But though the soil of the eastern slope is rich, the lack of transport makes it unproductive. It is this unexploited and almost impenetrable mountain region which so effectively cuts off the Amazon valley from the Pacific coast that it needs to be approached from the Atlantic side. We see in this great valley illimitable forests, yet all the timber used on the Pacific coast has to be imported from overseas. The collection of wild rubber has declined with the fall in the price of the marget commodity. About Iquitos in the upper waters of the Amazon lie an indefinite number of rich agricultural acres which, under happier geographical circumstances, could support a large population, yet there is at present no more than one human being to every two and a half square miles. Iquitos is over a month's journey by land from Lima, the capital of Peru, on the Pacific coast, and a voyage by sea, the Panama Canal and the Amazon from Callao to Iquitos, recently occupied a steamer no less than 80 days. The mountain barrier, which has remorselessly cut off the comparatively civilised coast from its hinterland by the Amazon, has set the white Peruvians an economic problem which is as yet far from solution.—*Board of Trade Journal.*

#### ON A RECENTLY FOUND METEORIC IRON FROM GLASGOW, BARREN COUNTY, KENTUCKY.

By GEORGE P. MERRILL.<sup>1</sup>

(From "*The American Journal of Science*," January, 1923.)

The iron meteorite briefly described below was first brought to my attention in

June, 1922, by Prof. Arthur M. Miller, of Lexington, Kentucky, by whom it has since been given a brief notice in *Science* for September 1, page 249.

According to Professor Miller, two pieces of the iron were found during the work of ploughing a field for three miles south-west of Glasgow, in Barren County. The pieces are stated to have weighed about 25 and 20 pounds respectively, and while very badly oxidised, exhibited on broken surfaces, even without etching, coarse Widmanstätten figures. The smaller of the two pieces was sent by Professor Miller to the National Museum, and it is upon this piece that the description here given is based. As received, the mass weighed but about 7 kilograms (15½ lbs.).

The iron is of the ordinary octahedral type, with kamacite lamina from 1 to 2 mm. in thickness, and is therefore classed as a coarse octahedrite. No troilite nodules are visible on the cut surface and neither tennite nor schreibersite are conspicuous. Plessite areas are small. The iron is in an advanced condition of oxidation that is difficult to arrest, suggestive of a high content of lawrencite. An analysis by Dr. J. E. Whitfield yielded:

	Per cent.
Iron .....	70.632
Nickel .....	7.270
Cobalt .....	0.620
Sulphur .....	0.110
Phosphorus .....	0.121
Carbon .....	0.062
Chlorine .....	0.363
Nickel iron oxides .....	19.220
Silica .....	Trace
Ignition .....	1.650
Total .....	100.048

Satisfactory chlorine determinations in meteoric irons are none too abundant. Cohen gives figures running from 0.003 to 1.48 per cent. There are reasons for supposing that the higher are not absolutely correct. Be this as it may, Whitfield's find of 0.363 per cent. Cl, equivalent to 0.623 per cent.  $\text{FeCl}_2$ , is high, and doubtless accounts for the too ready disintegration mentioned above.

U.S. National Museum,  
Washington, D.C.

<sup>1</sup> Published with the permission of the Secretary of the Smithsonian Institution.



## New Patents

This list is specially compiled for the *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

### Latest Patent Applications.

- 35356—Ashai Glass Co.—Forcing agent of manure. Dec. 29.  
3522—Edwards, G. W.—Treatment of oxidised copper ores. Dec. 27.  
35502—Therma; Industria & Chemica Research Co.—Apparatus for heat-treatment by molten metal. Dec. 20.

### Specifications Published this Week.

- 190212—Mond, A. L.—Process for the continuous leaching of ores, metallurgical products, and other materials on the counter-current principle.  
190246—Perkins, W. G.—Treatment of copper ores.  
190269—British Cellulose and Chemical Manufacturing Co.—Treatment of cellulose acetates.  
174041—L'Air Liquide Soc. Anon Pour L'etude et L'Exploitation Des Produits.—Apparatus for the synthesis of ammonia.  
190390—Bichowsky, F.—Processes for the synthetic production of alkali metal cyanides.

### Abstract Published this Week.

**Titanium-Nitrogen Compounds.**—Patent No. 188558.—Messrs. Bichowsky, F. von, and Hartham, J., of 1412, San Fernando Building, Glendale, California, U.S.A., have developed a process for the production of the above compounds. They are produced by heating a mixture of ilmenite, carbon, and an alkali-metal compound containing oxygen but not containing sulphur, in presence of nitrogen or gaseous mixtures containing the same, the temperature being slightly below the melting point of the mass. The carbon may be supplied as soot, coke, or a compound containing carbon, such as crude oil, and these materials may be supplemented, or even supplanted, by gaseous mixtures containing hydrocarbons, such as natural gas. In one example, 100 parts of finely ground ilmenite, 5 parts of anhydrous soda ash, and 10 parts of pitch are briquetted and heated under slight pressure for six hours in presence of natural gas containing 20 per cent. by volume of nitrogen. The temperature may be at first between 1,100–1,200° C., but is finally maintained at 1,000–1,100° C. to avoid melting the iron. The product is allowed to cool in an atmosphere of neutral gas, and the iron dissolved out with warm dilute sulphuric acid. Another example illustrates the use of crude oil tar as the reducing agent, and sodium silicate and soda ash as the alkali-metal compounds. The titanium nitride or cyanonitride obtained may be used for the preparation of ammonia, or directly as a fertiliser.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the official price of 1s. each.



## THE CHEMICAL NEWS,

VOL. CXXVI. No. 3277.

### BRITISH INDUSTRIES FAIR, 1923. VIII.—STATIONERY AND PRINTING SECTIONS.

The Paper, Printing, Stationery, and Office Appliance Sections of the Fair form one of the largest groups exhibiting, and all the various trades connected with these important industries will be well represented.

A well-known firm of paper makers will be exhibiting their noted tinted papers, which are guaranteed fast to light. This firm also make a speciality of coiled papers in all widths. Others will be showing a large range of papers and boards, together with manufactured stationery, and office furniture, while another leading firm, who have recently installed modern and complete plant for the purpose of manufacturing crepe papers of all kinds, including decorative crepe papers suitable for window dressing and all kinds of advertising matter, will display a complete range of their products.

In the Printing Section there will be a number of the large printing firms, embracing all the different processes of printing for the production of works of art, and commercial printing, such as catalogues, posters, etc.

The art of colour printing in the United Kingdom has of late years made so much progress that we may be said to be in advance of the whole world. In particular we are specially predominant in the three and four colour processes, and there are many firms with hundreds of pretty subjects in various sizes suitable for use as fancy box-tops, calendar tops, advertising showcard tops, as well as for framing or decorative purposes. The smaller nations have neither the means of producing good colour work nor the population that would make such production a commercial selling proposition; therefore, such goods are imported. Germany for many years did an enormous trade in cheap colour reproduction for the above purposes, but first cost of blockmaking and printing are so high now that German firms are largely selling old subjects.

United Kingdom firms are still publishing, and, bearing in mind the greater interest to the Empire of British scenes and subjects as against German designs, which usually show foreign figures and landscapes, many enquiries for these lines are anticipated.

## PLANNING COMMERCIAL VICTORIES.

### GREAT DISPLAY OF ELECTRICAL EXHIBITS AT WEMBLEY.

More than half the space available for electrical engineering exhibits at the British Empire Exhibition has been booked already.

In this section, with an area of 200,000 square feet, organised by the British Electrical and Allied Manufacturers' Association, there will be a mile of gangways for the visitor to walk, and nearly two miles of stand frontages to be visited.

The electrical industry is one of the youngest of the great industries of the world, but every year brings new inventions, developments and improvements, and in 1924 the public will realise as never before what this industry means and what it offers to them. It is clear that the organising minds intend to prove to the world that the capacities and resources of the industry are co-extensive with the Empire itself.

Women will be shown what electricity can do for them in their homes. Electric labour-saving devices, electrical appliances for the preparation and cooking of food, washers, cleaners, irons, kettles and the innumerable appurtenances of the modern home will be demonstrated in infinite variety.

Among the many exhibits of interest to the technical and non-technical visitor alike are:—

Electrical accessories, accumulators, alternators, bells, batteries, cables, carbons, controllers, condensers, dynamos, generators, high tension fuses, instruments, insulating materials, lamps, meters, magnets, motors, models of workshops, power plant, rotary converters, searchlights, switchgear, starters, telephones, turbines, transformers and wiring supplies.

The millions of visitors to Wembley will be shown that the British electrical industry possesses a technical ability and a manufacturing capacity which maintain the best traditions of British commerce, and an effort will be made to educate the public and to create in them the desire to possess the many advantages which the use of electricity holds out to them.

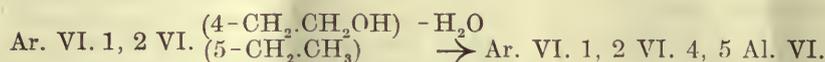
To set up this mighty monument of electrical achievement before the world for six months means that the industry is planning great commercial victories for the future.

## A NEW SYSTEM FOR THE LINEAR REPRESENTATION OF THE STRUCTURE OF ALL ORGANIC COMPOUNDS.

By T. SHERLOCK WHEELER, B.Sc.,  
A.R.C.Sc.I., A.I.C.

(Continued from Page 66.)

The system can be employed in writing equations. It can also be used in conjunction with our present system if it be desired to show the exact course of a reaction graphically, so that it may be apparent at a glance. Much space can be saved in this way, and there is no loss in clearness. The equation:—



illustrates this.

In some cases it may be desirable for didactic purposes to represent a chain as part of a closed ring. To indicate this, the compound is described as if the ring were closed, and the fact that one bond is missing is shown by a bar *underneath* the numbers of the two carbons which it would join.

The above description is sufficient to enable any possible type of ring compound to be described. One further example may be given: XVIII. is the probable formula of cinchonine. It is Al. VI. (N-4) 4, 1 VI. 3, 3' VI. (O-4) 5 II. 2 Ar. VI. (N-4) 5, 6 VI. The system is especially fitted for dealing with these polynuclear compounds so common in dye chemistry. Quinone, pyridine, thiophene, and such like structures are taken to come under the heading Ar, but if preferred Al can be placed before the symbols for the rings containing them and the double bonds indicated.

The following is a summary of the system:—

(i) A "structure line" is drawn, passing in ring compounds through the centres of rings and along chains joining rings. In open chain compounds the lines pass along the longest chains, and then along the branches; the longer branches are included as far as possible in the main structure line.

(ii) Rings are numbered clockwise from the extreme left-hand common carbon; chains are numbered in the direction of the structure line from where it joins them; common carbons are included in each ring and chain in which they occur.

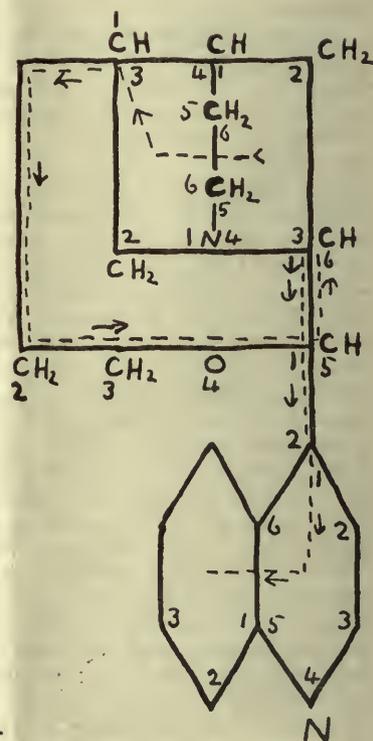
(iii) The number of elements in a ring is shown by plain Roman numerals; for a chain barred Roman numerals are employed.

(iv) All information about a ring or chain comes immediately after its Roman numeral, if possible; where it is necessary to refer back to any ring or chain, its symbol is labelled, so to speak, with an index.

(v) Substituents come after the number of the element to which they are attached; non-carbon elements precede the number of the place they occupy.

(vi) The extreme left and then the extreme right hand carbons common to two

rings are shown in that order, between the numerals for the rings by their numbers in



XVIII

the first ring. The single common carbons connected with chains are shown in a similar manner.

(vii) Ar. shows that the ring or rings following are aromatic, *i.e.*, can be written with a centric formula; Al. shows them alicyclic, *i.e.*, fully reduced.

(viii) A bar under the numbers of two carbons shows that the link joining them is to be removed after the compound is drawn as indicated.

(ix) Stereo-chemical terms are unaltered. Cis and trans come in between the representations of the groups or elements to which they refer. Fischer's system is used for indicating the orientation of asymmetric carbons in sugars, etc.; cis and trans compounds can also be shown on that system.

From the examples given, it will be seen that the system is capable of indicating any compound, no matter how complicated. In some cases the description is, of necessity, long, but it is never hard to unravel once the few simple rules are known. In fact after some little practice, the general structure of a compound is apparent at a glance from its description, while to describe a compound the structure line need never be more than drawn mentally. Where there are several ways of describing a compound on the system, the shortest is of course always to be preferred, and its use would be fixed in practice, but any of the ways available will yield up the formula when required. It is to be hoped that the scheme described will find a ready use in chemical dictionaries, chemical abstracts, chemical journals, and perhaps advanced text-books. In elementary text-books and all such cases where obviousness is of more importance than conciseness, the present day graphical formula would still, of course, want to be given directly; having to "translate" a concise but complete method of representation might perhaps confuse a beginner. Although the system does not seek in any sense to name the compounds described, yet it can be used as a basis of a system of nomenclature. This aspect of the matter will be dealt with later.

The author's thanks are due to Dr. A. M. Patterson, of Xenia, Ohio, for his helpful criticism of the above.

## NOTES ON THE ACTIVE PRINCIPLES OF SOME SOUTH AFRICAN PLANTS.

By CHARLES F. JURITZ, M.A., D.Sc.,  
F.R.S.S.A.F., F.I.C., CHIEF OF DIVISION OF  
CHEMISTRY, DEPARTMENT OF AGRICULTURE,  
UNION OF SOUTH AFRICA.

Up to the present, comparatively little investigation has been carried out by chemists in South Africa with relation to the active principles of South African plants. When I first drew public attention to the subject,<sup>1</sup> after alluding thereto more or less incidentally in many successive annual reports, practically no attention had been given to it outside South Africa, but to-day such names as those of Power, Salway, Rogerson, Tutin, Dunstan and Holmes testify to the interest which this branch of South African plant chemistry has aroused in other lands.

Within the borders of the Union of South Africa, however, the matter still stands near where it stood when I first voiced my plaint in 1905, and the *chemical* investigation of the poisonous and perhaps pharmacologically valuable principles of our flora scarcely advances further than the strict requirements of the courts of justice when Kaffir "medicine men" are being tried for culpable homicide.

Sixteen years have passed since the date of my first publication (alluded to above), and on four subsequent occasions<sup>2</sup> the great desirability of making a special feature of this phase of chemical research in South Africa has been strongly urged, but for a long time it seemed vainly. And yet it has not been altogether in vain: Dr. Rindl,

<sup>1</sup> "Some notes regarding South African Pharmacology," *Trans. S.A. Phil. Soc.*, Vol. XVI., pp. 111-113.

<sup>2</sup> R. Marloth, "The Chemistry of some vegetable products of South Africa," *C.G.H., Agricultural Journal*, 1909, pp. 634-638.

R. Marloth, "The Chemistry of South African plants and plant products," *Cape Chemical Society*, 1913.

C. F. Juritz, "South African plant poisons and their investigation," *Rept. S.A. Assoc. for Adv. of Science*, 1914, pp. 109-145.

C. F. Juritz, "The Urgency of a definite forward movement in the study of the active principles of South African plants," *S.A. Medical Record*, Nov. 13, 1915.

Professor of Chemistry at Grey University College, Bloemfontein, has definitely undertaken as a subject for research the study of South African pharmacology from a chemical standpoint, and a year or two ago Dr. J. W. C. Gunn was appointed Professor of Pharmacology at the University of Cape Town, and he has since undertaken systematic determination of the physiological action of plant substances peculiar to the flora of South Africa.

The facilities afforded by the establishment of a fully equipped Department of Pharmacology of the University in the vicinity of the laboratories of this Division in Cape Town, will enable the two institutions to co-operate in regard to the investigation of any plant supposed to be physiologically active: in fact, Prof. Gunn has already, in two cases, published the results of experiments which have been carried on in his laboratories, while such chemical work as has been possible was being performed in the laboratories of this Division. This will appear from the subjoined notes on three South African plants.

I.—WILD CELERY [*PEUCEDANUM GALBANUM* (L.)], BENTH. AND HOOK.

Some time ago statements regarding the therapeutic value of wild celery in cases of Bright's disease, and dropsy resulting therefrom, went the round of the South African press. Instances were quoted of persons who had suffered from the chronic disease for years, and had frequently been surgically tapped without more than temporary relief, but who had been restored to health after a few months' use of the above plant.

Dr. R. Marloth, in his "Dictionary of the Common Names of Plants,"<sup>3</sup> and also in his "Chemistry of South African plants and plant products,"<sup>4</sup> identifies this "wild celery" with *Peucedanum galbanum* (L.), Benth. & Hook (Natural Order Umbelliferae), and in the latter publication makes the following further reference to it:—

"The fresh plant contains a very volatile essential oil, which, when applied to the skin, causes severe dermatitis. Some persons are so sensitive that the mere touching of the leaves will produce blistering of the skin, generally about 30 or 40 hours afterwards, although the contact itself causes no irritation."

On account of this property the plant is also very well known under the name of "Blistering bush." It is common on the mountains around Cape Town, and an infusion of the leaves is largely used amongst the coloured classes of the peninsula as a diuretic.

An investigation of the fresh green leaves, kindly supplied by Mr. C. R. Ross, Conservator of Forests, Western Conservancy, was undertaken in the laboratories of the Division of Chemistry at Cape Town by Mr. W. J. Copenhagen, steam distillation of from 3 to 8 kilos. at a time being carried on for extraction of the volatile oil. The quantity of the latter obtained from the fresh leaves. It was light brown in colour, and possessed the strongly aromatic odour which characterises the plant. The following physical constants were found:

Specific gravity at 24° C. .... 0.847

Refractive index at 40° C. .... 1.4742

When the previously steam-distilled oil was collected and heated to 85° C., it distilled over, apparently breaking up simultaneously into fractions.

With a view to testing the supposed vesicant properties of the oil, it was applied to the arms of a number of persons without any irritating effect being noticeable, either immediately or after the lapse of time. The leaves, both fresh and dried, were similarly experimented with, also without any blistering effects.

In order to permit of more precise physiological tests, some of the volatile oil was sent from this laboratory to the Pharmacology Department of the University of Cape Town, and a note by Prof. J. W. C. Gunn and Dr. E. M. K. Geiling on their experiments with it was subsequently published in the *South African Medical Record*.<sup>5</sup> Some of their conclusions are here quoted:—

"The volatile oil . . . has a persistent nauseating taste, but is not specially irritating to the mucous membrane of the mouth or stomach. The oil was rubbed into the skin of several people,<sup>6</sup> but there was no sign of irritation apart from the initial redness caused by the rubbing. . . ."

"In our opinion, the irritant properties of the plant are not due to this volatile oil. The length of time that

<sup>5</sup> Vol. XVIII., 1920, p. 288.

<sup>6</sup> The authors are not referring here to the similar test previously applied in the laboratories of the Division of Chemistry.

<sup>3</sup> 1917, p. 19.

<sup>4</sup> 1913, p. 12.

elapses before the onset of dermatitis after contact with the plant points rather to some non-volatile constituent as the cause.

"An infusion of the plant is sometimes used as a diuretic. In this respect it is probably as efficient as buchu, and could be used as a cheap substitute for the latter, but its unpleasant taste and the difficulty in handling it are disadvantages."

There are several South African species of *Peucedanum*. Harvey and Sonder enumerate some two dozen (inclusive of *Bubon* and *Anethum*); and *P. galbanum* is by no means the only species which yields an essential oil. Dr. Marloth<sup>8</sup> states that the plant commonly known as wild parsley (*P. tenuifolium* Thumb.) has a similar effect to that produced by *P. galbanum*. *P. graveolens* (L.), Benth. & Hook, also yields a volatile oil (dill oil), and its fruit has for long been used as a drug, both the fruit and the extracted oil being employed as an aromatic stimulant. In this connection E. J. Parry says,<sup>9</sup> "If the fruits can be produced in quantity in Cape Colony, they should form a most useful source of supply." This remark seems to have been prompted in part by the fact that J. C. Umney found the fruits of plants grown in South Africa to be slightly larger in size than those grown in England, and to contain a slightly higher proportion of oil—11.6 per cent., as compared with 10.9 per cent.

## II.—SLANGKOP (*URGINEA MACROCENTRA*, BAKER):

A quantity of bulbs of a species of slangkop was brought to the laboratory by Mr. K. F. Wolff from Doornfontein, P.O. Wilhelmshof, Boshof, O.F.S., with the object of ascertaining its value as a tanning material. The poisonous qualities of some species of slangkop are well-known: after the dry season the first green vegetation to appear in sight is the young shoot of this plant; the sheep and goats nibble it off and die, and hence many thousands are said to be lost annually. Mr. Wolff thought that

if the bulbs could find useful application in the tanning industry, the country-side would simultaneously be delivered from a constant menace to stock-life.

There are several South African species of slangkop, or, as the genus called by that name in the Transvaal<sup>10</sup> is botanically known, *Urginea*. Not only are many species of this genus poisonous, but other genera of the Natural Order (Liliacæ), such as *Ornithogalum* and *Bowica*, have been partaken of with fatal effects either to man or stock. No less than 27 species of *Urginea* were enumerated by Thiselton-Dyer in *Flora Capensis* (Vol. VI., pp. 463-470). One of the best known species is *Urginea Burkei* Baker, commonly known as the Transvaal slangkop, and presenting to stock precisely the temptation already alluded to above. Of this plant Dr. Marloth says, "Nothing is known about its ingredients, and the antidotes employed are consequently quite empirical."<sup>11</sup> Then there are the purple slangkop, *U. sanguinea*, which is equally poisonous according to Dr. Marloth, and *U. altissima* Baker, or magerman, the bulb of which resembles the Mediterranean squill, *U. maritima* Baker, in its action.

*U. maritima*, which is found not only along the Mediterranean coast but also in the Cape Peninsula, contains a number of glucosides and other bitter principles, such as scillain or scillitin, and scillotoxin, belonging to the digitalis group, and producing effects somewhat similar to those of digitalis as heart poisons. In very small doses it is merely expectorant or diuretic, but in larger quantities it becomes emetic and purgative. For pharmaceutical purposes the bulb of this plant is divested of its dry membranous outer scales, cut into slices, dried, when it becomes brittle and is easily powdered. The dose is from 1 to 3 grains of the powder.

On *U. Burkei*, Mr. J. Burt-Davy wrote a short note in the *Journal of Industries*,<sup>12</sup> mentioning that the plant is acrid and poisonous, causing inflammation of stomach and intestines and paralysis. He also had a longer account of the plant in

<sup>7</sup> "Flora Capensis," Vol. II., pp. 553-561.

<sup>8</sup> "Dictionary of Common Names of plants," p. 66.

<sup>9</sup> "Chemistry of Essential Oils," 3rd ed., 1918, p. 294.

<sup>10</sup> The Cape slangkop is quite another plant—*Ornithoglossum glaucum*—which, however, is also poisonous.

<sup>11</sup> "Chemistry of South African plants and plant products": Cape Chemical Society, 1913, p. 5.

<sup>12</sup> Jan., 1920, p. 72.

the Report of the Transvaal Department of Agriculture for 1903-4, pp. 310-311, with three illustrations, dealing *inter alia* with the distribution of the plant, the season when it is most dangerous to stock, the symptoms of poisoning in stock, the local remedies, and other plants liable to be mistaken for slangkop.

The late Mr. L. H. Walsh, in his booklet on "South African Poisonous Plants," has two half-tone photographs of *U. Burkei*, with a description of the plant (pp. 31-32). "In Griqualand West and Bechuanaland," he says, "numbers of sheep die yearly from eating it, and in many districts of the Transvaal, notably Klerksdorp, its fatal properties are well known. . . .

After the early rains, the flower spike appears with the first green herbage, and is eaten by the hungry stock, while later the leaves make their appearance, and claim fresh victims." At the close of his note, Mr. Burt-Davy remarked, "If the active principle contained in *Urginea Burkei* should prove to be similar to that found in the squill, and of equal value, our native bulb might not only replace the imported drug, but might also become an article of export. Incidentally such commercial use of the plant would assist in clearing the country of a poisonous plant detrimental to the live-stock industry."

To return to *U. macrocentra*: the specimens sent to the Cape Town laboratory by Mr. Wolff were there examined by Mr. W. J. Copenhagen. The bulbs averaged 11 cm. in diameter and 380 gms. in weight. When fresh they contained 66.36 per cent. of moisture, and the proportion of tannin, determined by titration with potassium permanganate in the presence of indigo-carmin, <sup>13</sup> amounted to 0.53 per cent. of the fresh bulb. Obviously there is not much to be hoped for from such an article as a commercial tanning material. The bulbs were therefore minced and extracted, with a view to ascertaining their pharmacological potentialities. On extraction of the air-dried bulbs (containing 10.37 per cent. of moisture) with alcohol, after acidifying in the usual way, Mr. Copenhagen obtained 0.13 per cent. of the crude active principle. A 5 per cent. solution of this in 50 per cent. aqueous alcohol was prepared, and 1

cc. of this solution, injected subcutaneously into a guinea pig, caused death in from 7 to 10 minutes. This crude active principle formed precipitates with picric acid, gold chloride, and iodine in potassium iodide: it reduced Fehling's solution when boiled therewith.

The following colour-reactions were obtained:

Concentrated sulphuric acid—Brick red to violet.

Fröhde's reagent—Green.

Erdmann's reagent—Pink to red.

Mandelin's reagent—Red through pink to violet.

Sulphuric acid and potassium dichromate—Pink to dark brown.

Greenish<sup>14</sup> enumerates the following results of chemical investigations of squill, *U. scilla* Steinh. (*U. maritima* Baker):

"The constituents of squill [he says] are imperfectly known. Merck (1879) separated scillitoxin, scillipicrin, and scillin, all of which exhibit glucosidal properties. Scillitoxin and scillipicrin are both amorphous and act upon the heart, the former being the more active of the two; scillin is crystalline, but it is inactive. Scillain (Jarmerstedt, 1880) appears to be a purer form of scillitoxin. Waliszewski (1893) separated scillinin, schillipicrin and scillamarin. Kpaczewski (1914) isolated scillitin and scilli-diuretin; scillitin (0.2 to 0.37 per cent.) is an intensely bitter, purified form of scillitoxin and probably the active constituent in the purest condition yet obtained."

In order that the precise pharmacological action of the slangkop bulbs might be tested, some of the latter were supplied to Dr. J. W. C. Gunn, Professor of Pharmacology at the University of Cape Town. Prof. Gunn has recorded the results in his experiments in a paper read before the Royal Society of South Africa,<sup>15</sup> where he sums them up by saying that the action is the same as that of the digitalis bodies, a group which includes a number of substances of great medicinal value. Prof. Gunn thinks it possible that slangkop might replace squill in South Africa, and in fact may be found superior to the latter.

<sup>14</sup> "Text book of Materia Medica," 3rd ed., 1920, p. 388.

<sup>15</sup> Trans. Roy. Soc. S.A., Vol. IX., Pt. II., 1921, p. 197.

(To be Continued.)

<sup>13</sup> The method adopted in Leeds University Laboratory. H. R. Proctor: "Leather Industries Laboratory Book," 2nd ed., 1908, p. 227.

## THE FORTHCOMING "BUSINESS EFFICIENCY."

Now that, according to the highest authorities, trade is on the turn, and there are unmistakable signs in every direction that such is the case, business men all over the country will welcome the unique opportunity provided by "Business Efficiency" for witnessing all the latest scientific and labour-saving devices for facilitating business.

"Business Efficiency" is undoubtedly the greatest commercial education movement of the day, and will demonstrate how one man, with the aid of modern office appliances, can do the work of ten, how maximum efficiency can be secured at minimum cost, without interfering with existing organisations, and how by the introduction of better methods, success can be established to the utmost degree.

This epoch-making event, which has been promoted to help along the commerce of the country, will be of absorbing interest to every business man and woman. Assembled under one roof, at the Central Hall, Westminster, from February 7 to 17, will be found the world's most modern and approved methods for enabling business firms to turn out more work at less cost. Mr. Neville Chamberlain, M.P., Postmaster-General, will officially open "Business Efficiency" on February 7, at 12 o'clock.

In view of the increased cost of labour and overhead expenses, it was imperative that some move of this kind should be initiated, and as "Business Efficiency" was so successful in this direction last year, it was decided to continue it again on a far more extensive scale. Consequently more than double the accommodation has been reserved for this year's effort.

For the truth is that more than ever today the world wants better methods and better service. The business prizes go to those who are most efficient. Greater efficiency is what builds business in times like the present. The old threadbare ideas and antiquated methods will not suffice, and business men have got to keep up-to-date all the time.

"Business Efficiency" recognises that improved ideas have made the world what it is, and will shape the world of to-morrow. It is a co-operative effort of business men for the information of business people exclusively.

Experience has proved that the office is the brain system of every business firm; it is the nerve centre from which the executives direct and control the entire establishment, and when functioning on Business Efficiency lines radiates efficiency to every department. The great need for better methods in all administrative and executive departments of commerce is not fully appreciated. How to reduce unnecessary labour and increase individual and collective results is a problem every business man seeks to solve.

"Business Efficiency" shows how a far greater turnover can be secured for every individual firm, how the costs of production can be lowered in both office and works, and how future dividends can be paid out of savings. This is the psychological moment, when British trade is reviving, for business firms to take advantage of every possible appliance which will speed up production in every department.

There are devices to be exhibited which reveal a hundred and one ways of conducting business more efficiently and getting administrative work accurately and scientifically done. With the aid of these various appliances the amount of work the individual can do is enormously increased, and, many hours are thus saved from routine duties for more creative and profitable work.

The exhibits range from the very latest telephone system, by means of which two persons in different parts of an extensive building can speak to each other from whatever part of the room in which they happen to be without the necessity of raising the mouthpiece. This alone is a marvellous invention—worth going to see.

Another amazing example of efficiency is the latest calculating machine. In an instant, by a shuffle of the index cards, answers to every conceivable question relating to the customer can be obtained. Yet a further innovation is the complete office printer, which can be operated by junior clerks, and turns out every description of printing quickly at 50 per cent. less cost.

All the ingenious stamping contrivances, machines for protecting cheque-writers against fraud, all the modern systems of loose-leaf books, the latest carbons, ribbons, typewriters and recorders for checking piece work can be seen. In fact everything that can possibly release human brains and intelligence for work which is not mechani-

cal has been included, and the valuable time and expense thus saved to business firms is almost beyond calculation.

A word about the promoters—the Office Appliance Trades Association—whose membership consists of men who realise that the country's well-being greatly depends upon the advancement of efficiency in business.

The objects of the Association are the linking up of the activities of those industries which have already done so much to make business building and management easier and more harmonious, the spreading among British business people of further knowledge of commercial efficiency, and the general improvement of modern business conditions.

The Association makes no profit, for its members bear the expenses, and "Business Efficiency" is free to all desiring to improve their capacity for better business. Whatever the type of business, whether a one-man business or a gigantic organisation, "Business Efficiency" will show how things can be done better still. It will prove of invaluable benefit to the managing director, business organiser, business executive, manager, salesman, foreman, and all who are keen on the best methods for conducting business with efficiency and despatch.

More than ever to-day, the onus for the success of any business falls more heavily upon the individual member of the staff, in whatever capacity he happens to serve, and "Business Efficiency" is of vital interest to every business man. London's leading authorities on commercial efficiency will demonstrate the practical application of every new device, without any obligation, and admission is by invitation or presentation of business card.

To those desirous of forging ahead in business and anxious to take full advantage of every facility that will help in this direction, now that trade is on the turn, "Business Efficiency" provides a very real opportunity.

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL SOCIETY.

ORDINARY MEETING—JANUARY 18, 1923.  
*Sir Charles Sherrington, President, in the Chair.*

The following papers were read, the summaries here printed having been supplied

by the authors for use at the meeting:—

J. BARCROFT, F.R.S. *Observations on the Effect of High Altitude on the Physiological Processes of the Human Body.*

Three principal factors appear to have a positive influence in acclimatization:—

- (a) The increase in total ventilation, which usually raises the alveolar oxygen pressure ten or twelve millimetres higher than it would otherwise be;
- (b) The rise in the oxygen dissociation curve so that at any oxygen pressure the hæmoglobin will take up more oxygen than before;
- (c) The rise in the number of red corpuscles, and correspondingly in the quantity of hæmoglobin.

These factors were provisionally treated as independent variables. In reality they are not so, for blood can be made artificially to resemble high-altitude blood, by shaking out the CO<sub>2</sub> and then withdrawing a portion of the plasma, so that the blood is richer in corpuscles. Such blood has been found to give, at the alveolar CO<sub>2</sub> pressure of the Andes (27 mm. CO<sub>2</sub> or thereabouts):—

- (1) A reaction which is apparently almost unchanged, or even more acid, as measured by the ratio of combined to free CO<sub>2</sub>;
- (2) A more alkaline reaction by the platinum electrode;
- (3) An oxygen dissociation curve which rises apparently out of proportion to the change in reaction.

Herein would appear to be the essence of the acclimatory process. The possibility of the oxygen dissociation curve altering owing to a specific loss of CO<sub>2</sub> appears to be ruled out. There was an increase in the hæmoglobin value of the blood and in the red cell count in all cases. On making the ascent, there was a marked increase in the number of reticulated red cells, after the descent these cells fell to below their normal percentage. In the natives the ratio of reticulated to unreticulated red cells was not greatly increased, but the absolute number of reticulated cells per cubic millimetre was about 50 per cent. greater than normal. We argue a hypertrophy in the bone marrow. There were no nucleated red cells. The increase in red blood corpuscles is such as to cause an absolute increase in the amount of oxygen in each cubic centi-



metre of blood in the majority of cases, in spite of the decrease in saturation.

A number of mental tests of the ordinary type were performed at Cerro and at sea-level. These revealed no particular mental disability in the Andes, but, in our opinion, as well as in that of psychologists whom we have consulted, we have shown rather that our tests were inadequate than that our mental efficiency was unimpaired.

A number of tests were made for the purpose of discovering whether the pressure of oxygen in the blood was or was not higher than that in the alveolar air. In all cases they were so nearly the same that we attribute the passage of gas through the pulmonary epithelium to diffusion.

PROF. E. W. MACBRIDE, F.R.S. *Remarks on the Inheritance of Acquired Characters.* (Verbal communication only.)

It is well known to zoologists that during the last fifteen or twenty years a series of experiments have been carried out by Dr. Paul Kammerer at Vienna, which tend to show that acquired qualities or, in other words, modifications of structure induced by modified habits, are inheritable. The results of these experiments have been received with much scepticism, both here and on the Continent, and the *bona fides* of Dr. Kammerer has been called in question.

One of the most interesting of his experiments was in inducing *Alytes*, a toad which normally breeds on land, to breed in water. As a result, after two generations, the male *Alytes* developed a horny pad on the hand, to enable him to grasp his slippery partner.

It has been admitted by Kammerer's critics that if he could demonstrate this pad, he would to a large extent succeed in establishing the validity of his results.

This summer, at my request, Mr. J. Quastel, of Trinity College, Cambridge, when in Vienna, interviewed Kammerer, and was shown by him one of these modified males. Quastel photographed the animal, and enlargements from his photographs are now shown. Subsequently, at my request, the Zoological Society despatched Mr. E. Boulenger on a visit to Vienna. He, too, saw the modified male, and was assured by Przi Bram, the head of the Biological Institute, that all Kammerer's experiments had been done under his (Przi Bram's) supervision, and were perfectly genuine.

C. F. COOPER. *Baluchitherium osborni* (? syn. *Indricotherium turgaicum*, Borriss-

yak.) Communicated by Dr. A. S. Woodward, F.R.S.

*Baluchitherium mosborni* is an aberrant rhinoceros of such unusual size as to be apparently the largest known land mammal. The remains of this animal were first found in Baluchistan, and are described in the present Paper. Subsequently, further fragments have been found in Turkestan, and quite recently more material, as yet undescribed, in China.

While resembling the rhinoceroses more than any other of the Perissodactyla, *Baluchitherium* is still isolated and of uncertain zoological position. There are certain adaptations to weight which have brought about a superficial resemblance in some of the limb bones of elephants. There are also resemblances in some of the foot bones and neck vertebrae to those of the horse, which are less easily explained, except by the hypothesis that this form is descended from a small eocene form, *Tripolpus*, which likewise shows an intermingling of horse and rhinoceros characters. In some structures, notably the excavations of the vertebral canal to ensure a combination of lightness and strength, *Baluchitherium* stands alone among mammals.

J. A. GUNN and K. J. FRANKLIN. *The Sympathetic Innervation of the Vagina.* Communicated by Sir Charles Sherrington, P.R.S.

H. G. CANNON. *On the Metabolic Gradient of the Frog's Egg.* Communicated by Prof. E. W. MacBride, F.R.S.

BASISWAR SEN. *On the Relation between Permeability Variation and Plant Movements.* Communicated by Sir William Bayliss, F.R.S.

H. L. DUKE, M.D. *An Enquiry into an Outbreak of Human Trypanosomiasis in a "Glossina morsitans" Belt to the East of Mwanza, Tanganyika Territory.* Communicated by Mr. C. Dobell, F.R.S.

LOUIS DOLLO, Sc.D. *Le Centenaire des Iguanodons (1822-1922).* Communicated by Prof. A. C. Seward, F.R.S.

THURSDAY, JANUARY 25, 1923, AT 4.30 P.M.  
Papers read:—

PROF. A. V. HILL, F.R.S., *The Potential Difference occurring in a Donnan Equilibrium and the Theory of Colloidal Behaviour.*

E. F. ARMSTRONG, F.R.S., and T. P. HILDITCH, *A Study of Catalytic Actions at Solid Surfaces. X.—The Interaction of*

*Carbon Monoxide and Hydrogen as conditioned by nickel at relatively low Temperatures. A Practical Synthesis of Methane.*

J. HOLKER, D.Sc., *The Periodic Opacity of certain Colloids in progressively increasing Concentrations of Electrolytes.* Communicated by Prof. A. V. Hill, F.R.S.

E. K. RIDEAL and R. G. W. NORRISH, *The Photochemistry of Potassium Permanganate. Part I.—The Application of the Potentiometer to the Study of Photochemical Change. Part II.—On the Energetics of the Photo-decomposition of Potassium Permanganate.* Communicated by Sir William Pope, F.R.S.

E. A. FISHER, *Some Moisture Relations of Colloids. I.—A Comparative Study of the Rates of Evaporation of Water from Wool, Sand and Clay.* Communicated by Prof. A. Smithells, F.R.S.

R. WHYTLAW-GRAY, J. B. SPEAKMAN, and J. H. P. CAMPBELL, *Smokes, A Study of their Behaviour and a Method of Determining the Number of Particles they contain.* Communicated by Prof. A. Smithells, F.R.S.

R. WHYTLAW-GRAY and J. B. SPEAKMAN, *A Method of determining the Size of the Particles in Smokes. Part II.* Communicated by Prof. A. Smithells, F.R.S.

R. C. RAY, *The Effect of Long Grinding on Quartz (Silver Sand).* Communicated by Dr. M. W. Travers, F.R.S.

#### ABSTRACTS OF THE PROCEEDINGS OF THE GEOLOGICAL SOCIETY OF LONDON.

JANUARY 10, 1923.

Prof. E. J. Garwood, Sc.D., F.R.S., Vice-President; and afterwards Prof. A. C. Seward, Sc.D., F.R.S., President, in the chair.

PROF. WILLIAM JOHNSON SOLLAS, Sc.D., F.R.S., F.G.S., then proceeded to deliver a lecture on *Man and the Ice-Age*.

He said that, thanks to the researches of General de Lamothe, Prof. Depéret, and Dr. Gignoux, the Quaternary System now takes its place as a marine formation in the stratified series.

Four ancient coast-lines of remarkably constant height have been traced around the Mediterranean Sea and along the western shores of the North Atlantic Ocean.

These, with their associated sedimentary deposits, form the successive stages of the Quaternary System: namely, the Sicilian (coast-line about 100 metres); the Milazian (coast-line about 60 m.); the Tyrrhenian (coast-line about 30 m.); and the Monastirian (coast-line about 20 m.).

The Sicilian deposits rest unconformably upon the Calabrian (Upper Pliocene), and in their lower layers contain a characteristic cold fauna. The fauna of the Milazian is warm-temperate, of the Tyrrhenian and Monastirian still warmer, for they contain numerous species of mollusca which now live off the coast of Senegal and the Canary Islands.

The three lower coast-lines correspond with the three lower river-terraces of the Isser (Algeria), the Rhône, and the Somme. Hence it may be inferred that the position of the river-terraces has been determined by the height of the sea-level.

The lower gravels of the three lower terraces of the Somme all contain a warm fauna, *Elephas antiquus* and *Hippopotamus*, and thus (like the corresponding marine sediments) testify to a warm climate. The climate of the Quaternary age was, on the whole, warm-temperate or genial, but interrupted by comparatively short glacial intervals.

The outermost moraine (Mindel) of the Rhône Glacier is associated with the Milazian terrace, the intermediate moraine with the Tyrrhenian, and the innermost moraine (Würm) with the Monastirian; except for their serial order, these associations are (in a sense) accidental.

It is now possible to assign the Palæolithic stages of human industry to their place in the Quaternary System: thus the "Strepyan" or pre-Chellean is Milazian in age, the typical Chellean—Tyrrhenian, the evolved Chellean, Acheulean, and Lower Mousterian—early Monastirian, and the Upper Mousterian, Aurignacian, Solutrian, and Magdalenian—later Monastirian.

The coast-lines of the Northern Hemisphere appear to have their counterparts in the Southern Hemisphere, and the researches of Dr. T. O. Bosworth in Peru and Prof. G. A. F. Molengraaff in the East Indies have revealed extensive marine Quaternary deposits and successive movements of the sea-level.

The Quaternary movements are probably due to a general deformation of the globe involving eustatic changes in the level of the sea.

The lecture was followed by an interesting discussion, in which the following gentlemen took part: Mr. W. Whitaker, Mr. Walter Johnson, Mr. S. H. Warren, Prof. J. E. Marr, Prof. P. G. H. Boswell, Mr. H. Dewey, Mr. K. S. Sandford, and the Secretary.

At the meeting on Wednesday, February 7, a lecture on the "Geological Results of the Shackleton-Rowett (*Quest*) Expedition" will be delivered by Mr. G. Vibart Douglas, Geologist to that Expedition.

The Annual General Meeting of the Society will be held on Friday, February 16, at 3 p.m. The Fellows of the Society and their friends will line at the Cafe Royal (Regent Street, W.1) on the same day, at 7.15 for 7.30 o'clock.

#### ROYAL INSTITUTION.

On Tuesday, January 30, at 3 o'clock, Mr. R. D. Oldham began a course of two lectures at the Royal Institution on "The Character and Cause of Earthquakes"; on Thursday, February 1, Professor I. M. Heilbron delivered the first of two lectures on "The Photosynthesis of Plant Products," and on Saturday, February 3, Mr. J. C. Squire, Editor of the *London Mercury*, commences a course of two lectures on "Subject in Poetry," with special reference to contemporary practice. The Friday evening discourse on February 2 will be delivered by Mr. C. F. Cross, on "Fact and Phantasy in Industrial Science," and on February 9 by Sir John Russell on "Rothamsted" and Agricultural Science.

#### THE SOCIETY OF DYERS AND COLOURISTS.

A meeting of the Manchester Section of the Society was held on January 19, when two papers of great interest were read. Mr. William Marshall, J.P., F.I.C., F.C.S., presided.

*The Behaviour of Titanic Acid towards Dyestuffs*, by J. K. Wood, D.Sc., F.I.C., and A. M. MORLEY, M.Sc.TECH., A.I.C.

Dr. Wood, in reading the above-titled paper, said the element titanium occurs in the fourth group of the periodic classification, together with silicon, zirconium, tin, and other elements. These elements form hydroxides which are amphoteric in char-

acter, and which are commonly referred to as acids. It has been customary to consider these substances as capable of existing in two modifications, known respectively as alpha and beta acids, and showing a considerable difference in behaviour towards reagents. Although the practice has been to speak of only two varieties of the various acids, the facts recorded in the literature would suggest that more than two modifications are obtainable according to the methods of preparation which are employed. It is, however, extremely doubtful whether the substances referred to are definite hydrates of the oxide of the elements in question, and the opinion has gained ground in recent years that the difference between the so-called modifications of these acids is really due to a difference in size of their primary particles. The ortho acid, now commonly referred to as the alpha variety, is considered to exist in the form of small particles which are more readily attacked by reagents than the larger and more complex of the meta, or, as it is now commonly called, the beta acid. If the difference in property is really due to the size of the particles, it will be seen that this opens up the possibility of the existence of a number of modifications of the acids which would be in harmony with the behaviour as recorded in the literature. It has long been known that it is possible for the alpha modifications of these acids to be transformed into the beta varieties, and that, in turn, the beta may, under certain conditions, be re-converted into the alpha varieties, but no definite explanation of these changes and of the causes which operate to bring them about was offered until a few months ago, when, as the result of experiments on the stannic acids, Mr. Collins and himself suggested that the gradual change in the structure and properties of these properties might be traced to the amphoteric character of the oxides in question.

Mr. Collins and himself showed by papers published last year that the hypothesis is in agreement with the behaviour of Stannic Acids under varying conditions, and they also suggested that the isomerism of the analogous compounds of titanium, zirconium, and other elements, might be similarly accounted for. Numerous experiments which have been made with Mr. Morley show that this supposition that the explanation of the isomerism of the titanio acids was due to a similar cause is justified,

so that in regard to titanium hydroxide or titanio acids it may be assumed that between the so-called alpha titanio acid and the beta titanio acid, just as with Stannic Acids, there is a series of substances of gradually increasing complexity of their ultimate particles, and that there is really a continuous series of these substances gradually increasing in beta character as a process of condensation takes place as the result of the titanium hydroxide functioning in two capacities. This was more or less a theoretical statement which it was necessary to bear in mind with regard to the present position of knowledge regarding these so-called isomeric acids. One result of a process of condensation would be the gradual decrease in the total surface of the particles, because by the fusion owing to the process of condensation of several simple particles together, a complex particle was created, which must have a smaller surface than those from which it had been formed. Inasmuch as adsorption is a surface phenomenon it will be anticipated that, other things being equal, a sample of titanio acid having a pronounced beta character would possess a smaller adsorptive capacity than one in which the process of condensation had proceeded to a lesser degree.

A considerable number of experiments in support of the authors' deductions were explained.

*Investigations on the Constituents of Raw Cotton, IV.*, by PROFESSOR E. KNECHT, PH.D., M.Sc.TECH., F.I.C., and G. H. STREAT, M.Sc.TECH.

This paper was then read by Dr. Knecht, who stated that the title of the paper was rather a comprehensive one. It was really a second communication on cotton wax. In an account of the systematic extraction of the bleached cotton yarn which had been heated for 336 hours in a sealed tube at 93°, it was stated that the benzene extracted amounted to 0.3, alcohol 0.6, and water also 0.6 per cent. A partial confirmation of the assumption that these extracts were due to treatment in bleaching was obtained at the time by extracting some grey Egyptian yarn to exhaustion with benzene, then bleaching it, and extracting again with benzene, when a not inconsiderable further extract was obtained. The experiment was repeated later by Fernandez, and it was found not only benzene but also alcohol and water gave further ex-

tracts after bleaching. It was further ascertained that cotton which had been thoroughly bleached yielded, after being smashed to powder on an anvil, considerable amounts of extracts. Further work on this subject had now been carried out, and the results generally confirm those previously obtained. Briefly stated, the experiments showed that extraction of the raw cotton with benzene only removed the wax to the extent of about one-half, but that if the fibre substance is destroyed or disintegrated by chemical or mechanical means, the whole of the wax can be extracted, and is then found to amount to somewhat over one per cent. A further examination of cotton wax has revealed the presence of what appears to be another definite compound which differs in solubility, melting point, and composition from that described by Schunck.

#### GENERAL NOTES.

Abstract of evidence given before the Therm Charges Committee by the Assistant Secretary of the Institute of Chemistry (Mr. G. S. W. Marlow, B.Sc., F.I.C.), on behalf of the Council of the Institute of Chemistry and of the Board of the Institute of Physics:

The Assistant Secretary gave evidence in support of a memorandum presented by the Councils of both Institutes, which urged the authorities concerned to require that the qualifications of gas examiners should be defined, and suggested (in brief), (a) that evidence of attainment should be the possession of Fellowship or Associateship of one of the Institutes, of a University degree or equivalent diploma in chemistry and physics, or an engineering diploma with evidence of adequate training in those subjects; (b) that examiners should have had training and experience in gas examination; (c) that examiners should be members of a reputable body of chemists, engineers, or physicists.

He emphasised the importance in the public interests of the provision in the Gas Regulation Act as to the competence and impartiality of the gas examiners. He pointed out, however, that there was no provision in the Act for a definition of competence and impartiality, and that gas examiners were appointed by local authorities who, in many cases, were not compe-

tent to judge of the qualifications required of gas examiners. He then related the endeavours the Institute of Chemistry had made in 1920, whilst the Bill was before the House of Commons, to ensure the insertion into the Act of such definition, and related further that the Institute had been unsuccessful even in persuading the Board of Trade to give an indication of the nature of the qualifications required.

He referred to the fact that the Gas Referees, who had power only to advise, had issued a memorandum for the information of local authorities, in which some guidance as to competence and impartiality had been given, but he remarked that this memorandum contained phrases which lacked definition, and therefore the Institutes of Chemistry and of Physics had endeavoured to provide the necessary definition.

He then reviewed some of the appointments which had already been made, with a view to showing that local authorities had in some cases made unsuitable appointments. With regard to the appointment of whole-time officers of the authorities (such as medical officers of health, inspectors of weights and measures) he suggested that it was undesirable in the public interests that an officer should be appointed who *prima facie* was not competent, even though personally he might possess qualifications which might be deemed sufficient, since the psychological effect, upon the public, of indubitable evidence of competence was important. Moreover, such persons could not be considered impartial since in cases of doubt they would be biassed towards giving a satisfactory report in view of the fact that failure to maintain an adverse report might possibly endanger their major appointments.

He also criticised cases in which local authorities had advertised appointments to tender, and suggested that persons of good professional standing would be unlikely to apply under such conditions.

In further criticism of certain aspects of the Act, he suggested that it was not in accordance with the public interests that the gas examiners should be required in certain cases to give notice to the gas companies of the time at which they proposed to make a test, and further that for the good administration of the Act, it was desirable that provision should be made for separate "lock-up" testing stations, so that there might be no doubt as to whether instruments had been tampered with.

In conclusion, he drew particular attention to the desirability of gas examiners being members of reputable professional bodies which had strict rules of professional conduct, and could exercise penal powers upon examiners who were guilty of partiality.

In reply to members of the Committee, the Assistant Secretary remarked that in order that provision might be made for such regulations as to competency, the Act would require amendment, and he suggested that the Board of Trade or the Gas Referees should be given powers similar to those possessed, say, by the Ministry of Health, in the case of public analysts under the Sale of Foods and Drugs Act, to prescribe regulations as to competency.

He agreed that it would be possible to arrange for the *ad hoc* examination of candidates for posts as gas examiners, such examination to be conducted under the auspices of the Institutes, or alternatively to provide for the recognition of existing examinations.

In the subsequent evidence of witnesses, particularly that of Mr. Butterfield, a Gas Referee, it was clear that the Committee had grasped the importance of the question of the competency and impartiality of the examiners, and also of the other matters mentioned in evidence.

The Chairman of the Committee remarked to Mr. Butterfield that the very wide powers given to the Gas Referees appeared to be rendered void in certain cases, since there was nobody who had a power of veto upon the appointment of incompetent examiners.

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#### TO LIGHT A TOWN OF 100,000 INHABITANTS.

B.E.A.M.A.'s £130,000 OFFER OF POWER  
STATION AND PLANT AT WEMBLEY.

From one source alone, enough electric power to light a town of 100,000 inhabitants will be supplied to the British Empire Exhibition at Wembley.

We are officially informed that the Council of the British Electrical and Allied Manufacturers' Association have offered to supply to the Exhibition a temporary power station, the value of the plant for which amounts to about £130,000. The turbine station will be complete with switchboards and sub-stations. They are

also prepared to supply additional generating plant, if required, amounting in value to over £50,000. This plant will be lent to the Exhibition on terms representing only a small fraction of its value.

The power generated in this station would supply a town of 100,000 inhabitants, or it would light a 60-watt lamp every hundred yards on the road from London to Glasgow.

The blades of the turbines will revolve at a speed of five miles a minute. While the exhibition is open they will travel a distance which would enable the world to be traversed and every dominion in the Empire to be visited no fewer than twenty times; while those more venturesome than Jules Verne could travel to the moon and back.

Enough steam will be evaporated in the power station to flood the stadium to such an extent that the cup finalists would have to play the game up to their knees in water.

Coal to be consumed, if brought in one load, would require a train over two miles long.

#### UNIVERSITY OF PRAGUE.

An interesting ceremony took place on January 8, 1923, at the Promotion Hall of the Bohemian (Charles) University, when the degree of Doctor of Natural Science was conferred by Professor J. Štěrba-Böhm upon Mr. J. G. F. Druce, M.Sc., of London.

Mr. Druce had presented a Thesis entitled, "Contributions to the Chemistry of Organic Tin Compounds." This was accepted, and Mr. Druce was called to the "rigorosum" and was examined in General, Physical, and Inorganic Chemistry and in Botany, the examinations being conducted in English and French.

Mr. Druce satisfied the examiners, and passed with distinction, and thus has the honour to be the first Englishman to obtain this degree.

In his speech acknowledging the honour conferred upon him, Mr. Druce referred to the achievements of Bohemian scientists, mentioning the researches of Professor B. Brauner upon Atomic Weight determinations and other important investigations in Inorganic Chemistry. He hoped that other English students would visit the Bohemian University, and that Czech students would

visit the Universities of England. In this way the scientists of both countries would in future benefit by this exchange. The Rector of the University (Professor Horáček) and the Dean of the Faculty of Science (Professor Domin) expressed similar sentiments and hopes.

#### HYDROXY STEARIC ACID.

By L. G. RADCLIFFE AND W. GIBSON.

Hydroxy stearic acid is the product formed when oleic acid is sulphonated, and by appropriate treatment including recrystallisation from alcohol, the acid is obtained as crystals M.P. 81°-82° C. Both methyl and ethyl esters can be prepared by treating the hydroxystearic with the necessary alcohol (pure) and dry hydrogen chloride. Methyl ester M.P. 46° C. and ethyl ester 48.5° C. On acetylation, the acid gives a white powder, M.P. 31-32° C. Attempts to prepare a nitro derivative of stearic acid by treating bromo-stearic acid with silver nitrate in alcoholic solution were unsuccessful. Direct nitration of hydroxystearic acid gave a greenish yellow crystalline product, M.P. 83-83.5° C., and containing no nitrogen. No formula can be suggested for this unknown acid. Other nitration products are a yellow oil and a white crystalline solid, M.P. 80-120° C.—(*J. Soc. Dyers Col.*, 1923, p. 4.)

#### REVIEWS ON

CAROTINOIDS AND RELATED PIGMENTS.

YEAR-BOOK OF PHARMACY, 1922.

DICTIONARY OF APPLIED CHEMISTRY.

By John Missenden.

*Carotinoids and Related Pigments: The Chromolipoids*, by LEROY S. PALMER, PH.D. Pp. 316. New York: The Chemical Catalog Co. Inc., 19, East 24th Street. Price \$4.50.

This interesting treatise does not, as do so many volumes of a similar order, deal solely with the phytochemical aspects of the yellow-to-red colours, but also incorporates the carotinoids obtained from or contained in the vertebrates or invertebrates. The author has wisely followed M. Towett's suggested form of classification, thereby maintaining a consistency well in keeping with a difficult series of compounds. Towett divided the carotinoids

into two categories; the carotins (*i.e.*, substances identical or isomeric with carotin,  $C_{40}H_{56}$ \*), and the xanthophylls (*i.e.*, substances chemically related to carotin).

Extensive lists showing the organic origins of the carotins and xanthophylls have been introduced, as well as a list demonstrating the sources of both in the same plant or tissue. They are very exhaustive, and improvements upon them are scarcely possible. Considerable attention has also been paid to the comparison between the flower xanthophylls and those contained in the yolks of eggs and the blood-serum of fowls; and Schunk's spectroscopic investigations have been specially quoted. Spectrophotographs illustrating the wavelengths of absorption bands of both carotin and xanthophyll in various solvents have been reproduced. At the end of the volume are comprehensive indices showing authorities mentioned and subjects dealt with.

There is one great fault with the work: it is insufficiently classified. Reference is difficult, and the general arrangement would, perhaps, prove slightly monotonous to the student. It is very exhaustive, however, and the reasoning is clear and sound. Above all, records of research are strictly up-to-date, references having been made to studies as late as last year; for example, Hashimoto's "Carotinoid pigmentation of the skin resulting from a vegetarian diet" (*Journ. Amer. Med. Assoc.*, LXXVIII., 1111). As a complete review of all that is at present known of the carotinoids, no better treatise could be compiled, and it is to be hoped that the author will endeavour to facilitate reference through the text in future editions.

J.M.

\* Willstätter and Mieg.

*Year-Book of Pharmacy and Transactions of the British Pharmaceutical Conference, 1922.* London: J. & A. Churchill, 7, Great Marlborough Street, W.C. Price 12s. 6d.

This book has again been produced, and again it brings up to date investigations made during a year in pharmacy and chemistry. The three editors, J. O. Braithwaite (Abstracts from Papers), Thos. Stephenson, F.R.S.E. (New Remedies), and C. H. Hampshire, B.Sc., F.I.C., are to be congratulated upon the discriminative care they have exercised in their respective compilations.

Copious revisionary notes have been added to the abstracts, and cover every

branch of the year's research that has passed the cognisance of the Society. Special recognition is due to the numerous suggestions contained in the dispensing section, emphasis having been laid upon the rendering of precipitates easily diffusible. Among the papers read during the course of the conference are included three of inestimable importance, "Some Characteristics of Wheat-Starch," by T. E. Wallis, B.Sc. (Lond.), F.I.C.; "A Simple Instrument for taking Refractive Indices of Liquids," by R. Fouracre, Ph.C., F.S.M.C.; and "The Extraction of Quinine and Strychnine from Solutions of varying Hydrogen Ion Concentration: A Method for the Separation of Strychnine from Quinine," by Norman Evers, B.Sc., F.I.C.

The annual report showed an increase in membership for the Society, and a scheme was recommended for Committee reorganisation. The book not only shows itself invaluable and indispensable to existing members, but should certainly be on the bookshelf of every enterprising pharmacologist.

J.M.

*A Dictionary of Applied Chemistry, Vol. IV.,* by Sir EDWARD THORPE, C.B., LL.D., F.R.S. Pp. VIII. + 740. London: Longmans, Green & Co., 39, Paternoster Row, E.C.4. 1922. Price £3.

This volume covers the ground between L-acid and Oxydisilin, and incorporates the results of later research in every branch of Chemistry in this section. Many prominent chemists have contributed to it, each one an authority upon his particular subject.

Specific attention has been paid to substances of wide commercial utility and of pharmacological urgency. This is quite notable, as, in the construction of a work of this description, such a broad outline is seldom attained.

Two interesting papers, one upon Matches and the other upon Leather, typify the tone of the work. These papers not only give data solely from a theoretical standpoint, but also treat at some length with the practical sides. Extensiveness has been accorded such subjects as the Lactones, Logwood, Metallography, Methyl, the Naphthalenes, Essential Oils, and Opium. This is but a cursory selection, and a number of others, well worthy of eulogistic mention, could be quoted.

Even as a separate factor, the volume is admirable; but as one of a series, it is ex-

emplary. Considering, too, the excellence of the information it contains, its price is most reasonable, and in no way to be regarded as a bad investment by those who require a complete survey of every by-way in Chemistry. J.M.

#### NOTICES OF BOOKS.

*Text Book of Inorganic Chemistry*, by DR. J. NEWTON FRIEND, D.Sc., Ph.D., F.I.C., Carnegie Gold Medallist. Pp. XXV. + 367. Second Edition, volume IX., Part I. London: Messrs. Charles Griffin & Co., Ltd., Exeter Street, Strand. 1922. Price 18s.

It is gratifying to find that a second edition of such a book of reference as this by Dr. Friend has been called for. It indicates that this series of text books supplies a real need.

Most of the few errors that crept into the first edition have been corrected, and a summary of the dates of issue of the more important journals has been introduced.

It may be noted that the equation given on page 233 for the preparation of Osmium cyanide, does not balance.

Among the many and useful tables given is the number of nickel coins cast in various countries. The information contained therein may be trustworthy, but it would be interesting to know who is responsible for giving the currency of U.S.A., as paras and centesimos!

This volume, together with the others in the series, will be widely consulted and used by students and also by experienced workers.

*Bleaching Powder and its Action in Bleaching*, by R. L. TAYLOR, F.I.C. Pp. 79. Manchester and London: John Heywood, Ltd. 1922. Price 4s. 6d.

Mr. Taylor's book has been based upon his contributions to the theory and practice of Bleaching, since 1910. These are reproduced almost in the form in which they originally appeared, in chronological order, and include the author's important investigations on other action of carbon dioxide and of dilute acids on bleaching powder and on hypochloric acid, and on other branches of the subject as well.

It will be a convenience for students and others to have this information in a permanent form.



THIS list is specially compiled for the *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

#### Latest Patent Applications.

- 49—Bader, T.—Treatment of cellulose-acetate products. Jan. 1.  
78—Metals Production, Ltd.—Leaching copper ores containing slimes. Jan. 1.  
478—Nicholson, W. E.—Manufacture of sulphuric acid. Jan. 5.

#### Specifications Published this Week.

- 190553—Dunstan, A. E., Remfry, F.G.P.—Treatment of petroleum and other liquid hydrocarbons.  
169725—Wendel et Cie Les Petits Fils De F. De.—Receptacles for the transportation and preservation of air or other gases in the liquefied state.  
174595—Akt-Ges Fur Anilin Fabrikation.—Process dyeing skins, hairs, and the like.  
190688—Jacobson, B. H.—Manufacture of anhydrous metal chlorides.

#### Abstract Published this Week.

*Organic Mercury Compounds.*—Patent No. 188376.—Messrs. Fahlberg-List & Co., of 57, Alt Salbke, Sudost, Magdeburg, Prussia, Germany, have evolved a new process for the production of aromatic mercury cyanide compounds.

They are prepared by treating complex mercury compounds of phenol and its homologues with alkali cyanides in aqueous solution, or by heating phenol and its homologues with mercury cyanide in alkaline solution or with mercuric oxide in alkali cyanide solution. The products are efficacious against plant diseases. According to examples (1) mercury cresol cyanide is obtained by dissolving mercuric oxide in dilute sulphuric acid, adding o-cresol, boiling the resulting precipitate with sodium cyanide solution and evaporating the filtrate in vacuo; (2) o-cresol is boiled with mercury cyanide and dilute sodium hydroxide, and the mercury cresol cyanide separated by carbon dioxide or dilute acids; (3) mercury phenol cyanide is prepared by boiling phenol with mercuric oxide in sodium cyanide solution and treating the cooled solution with carbon dioxide or dilute acids.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the official price of 1s. each.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3278

## THE ISOLATION OF THE OXIDE OF THE NEW ELEMENT.

At the meeting of the Chemical Society on February 1, 1923, Dr. Alexander Scott delivered a paper on "A New Element belonging to the Fourth Group of the Periodic System." Its oxide resembled those of Titanium and Zirconium.

He had discovered it in a black sand from New Zealand, where large quantities may be obtained. Upon analysis, Dr. Scott found that this sand gave a residue insoluble in sodium hydrate. The residue was partially attacked by sodium bisulphate.

By this treatment about 1.4 grams of a solid resembling titanium dioxide were obtained. It was difficult, however, to discover a method for the determination of the equivalent of the metal which did not form salts readily.

It was eventually converted into the double potassium fluoride by treatment with potassium carbonate and hydrofluoric acid.

Dr. Scott announced that during the day (February 1) he had completed two analyses of this double fluoride.

He found that 0.7203 gram of the salt,  $K_2XF_6$ , gave 0.4507 gram of the oxide,  $XO_2$ . This result, the sum of two determinations, indicated that the element had an atomic weight of 175, corresponding with an atomic number of 72.

The element is thus identical with that announced by D. Coster and G. von Hevesy from the results of their examination of the spectra of certain zirconium ores.

Its oxide,  $XO_2$ , which was exhibited with specimens of the sand, was cinnamon brown in colour, which Dr. Scott stated might be due to a very minute trace of ferric oxide. He said that whilst the investigators in Denmark had only observed the spectrum of what they termed Hufnium, he had actually a quantity of the oxide.

Sir William Tilden, F.R.S., who presided, stated that Dr. Scott's discovery was a very remarkable one. It was, perhaps, noteworthy that few discoveries of new elements had been communicated to the

Chemical Society. Thus when Sir William Crookes discovered thallium in 1862, he naturally announced his discovery in *The Chemical News*.

Prof. H. E. Armstrong, who also rose to congratulate Dr. Scott upon his great achievement, hoped that a more appropriate name could be given to it. It was a difficult question to settle the point as to who had actually discovered the new element. It had developed from the application of Moseley's method, whereby we knew there was a blank at the position 72.

Prof. Smithells, who conveyed the congratulations of the country Fellows to Dr. Scott, pointed out that this was the first case of the discovery of an element which had actually been looked for and found.

At the same meeting of the Chemical Society, two other papers were read:

"The Derivatives of Tetrahydrocarbazole," Part II., by W. H. Perkin and S. G. P. Plant, and "The Chemistry of Polycyclic Structures in relation to their Homocyclic Unsaturated Isomerides," Part IV., by C. K. Ingold, E. A. Seeley, and J. F. Thorpe.

## A NATIONAL ASSET.

### THE ROMANCE OF A WAR WINNING INDUSTRY.

By Colonel Sir Arthur Holbrook, M.P.

Gas has proved such a useful servant to the general public that the present seems an opportune time to state a few facts which stand to the credit of the much maligned gas undertakings. Eleven years ago, the centenary of gas as an illuminant was celebrated, and during the whole of that period its history was one of progress from public want to public want. Previous to that our harder living forebears had been more or less content with hard-won sparks from the chafing of flint and steel for the lighting of rush-lights and candles. The clergy of many churches preached against the introduction of gas into churches as "profane and contrary to God's laws."

But gas lived down all this opposition and became what it is to-day, an indispensable adjunct to our very existence. And the reason for this lies on the surface: the needs of the community have been studied by the great industry. During the whole period of more than a century's service to the public, the best brains of the industry

have been engaged on improving methods of supply and cheapening costs.

Modern science has revolutionised the gas industry out of all recognition, and in doing so has, to a large extent, revolutionised the homes of the people by adding to their comfort, cleanliness, and convenience. Few people appreciate the national value of the 1,600 gas undertakings. The country has, perhaps, no greater asset. Time was when the carbonisation of coal was carried out with only one objective—production of ags. To-day there is hardly any trade or manufacture in which is not used some substance or another produced by the distillation of coal at the gas works.

Precisely how vital and how necessary the gas undertakings of this country are was demonstrated during the war, and it can be truthfully said that no industry more than the gas industry helped to win the war. The products of gas works and gas ovens saved the Allies. This assistance took the form of the production of such necessary products as benzol and toluol for the manufacture of high explosives, dyes and motor spirit, sulphate of ammonia, creosote, tar, and carbolic. During the war one gas undertaking alone supplied enough T.N.T. material for the manufacture of lyddite and other explosives to fill 160,000,000 18-pounder shells, 17,000,000 gallons of oil, and 13,000 tons of disinfectants. The total for the whole industry ran into figures representing six times these gigantic totals.

And gas has its uses in peace no less than in war, altogether apart from its domestic utility. Germany built up her great dye industry by working up the by-products largely obtained from England, and the dyes resulting from these by-products were purchased by the rest of the world from Germany, who reaped a rich annual harvest of many millions.

If England's dye industry and chemical trades are to be kept in existence, the gas industry must flourish. Out of smaller services rendered to the State, many other industries have reached the peak of prosperity. Not so the British gas undertakings, which were seriously handicapped during the war and have had tardy help since to recover their lost ground.

But few people realise how closely coal distillation is bound up with food production. Vegetables cannot live without a proper supply of nitrogen, and before the war this country imported large quantities

of nitrate of soda for this and other purposes. This supply was cut off during the war, so the gas works produced increased quantities of sulphate of ammonia, which serves the same useful purpose. Without this sulphate, grass and grain fields would yield but very poor results, and that would mean much less meat and corn for consumption.

Allotment holders are indebted to gas works for the gas lime which is so detrimental to the destructive wire-worms. Then there is naphthalene, which proved a God-send to the men at the front by helping them to exterminate lice and other vermin. And when "Tommy" went into hospital there came to his aid the products of the gas works in the shape of aspirin, phenacetin, and antipyrine, for all of which coal-tar from the gas works is responsible. Other friends in every-day life which emanate from the gas works include sulphonal for sleeping purposes, sal-volatile, carbolic acid, lysol, and such like useful things.

And so the wonderful story of a thousand and one uses of gas and gas products goes on. It is a worthy record, and the end is not yet, for the industry is always striving to keep abreast with modern requirements, and to raise the standard of efficiency. The gas industry did not fail the nation during the war, and will not fail the nation in the piping times of peace. Given fair play—it asks no favour—its history, as of old, will be one of progress from public want to public want.

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#### EMPIRE'S RESOURCES IN THE LESS COMMON METALS.

Professor G. T. Morgan, head of the Chemical Department of the University of Birmingham, is the President of the Chemical Society of that University, and on Monday, January 22, he delivered his Presidential address on "The Empire's Resources in the Less Common Metals." The attendance, which numbered over 200, included many industrial chemists of Birmingham and the Midlands.

The author observed that in his Presidential address of last year he placed before the Society a survey of the post-war problems affecting the synthetic colour industry. The chief reason why this branch of chemical enterprise has become a so-called "key" industry is, in his opinion, an

educational one. A highly developed industry in coal tar products leads with un-failing certainty to proficiency in other chemical arts. The inter-dependence of all branches of chemical trade has been demonstrated up to the hilt by the development of chemical industry in Germany, a country where faith in the possibilities of chemical development is far more generally accepted than in any other civilised nation.

The great Rhenish firms are something more than commercial undertakings, they are technological universities of the highest grade. It is largely owing to the educational leaven of these scientifically directed enterprises that Germany has gained her supremacy and prosperity in the main branches of chemical industry. The utilisation of atmospheric nitrogen, many modern metallurgical processes, scientific glassware, synthetic rubber and the highly profitable trades in drugs, photographic chemicals, synthetic tanning materials, artificial resins, synthetic essences and other fine chemicals have arisen as off-shoots of the scientific industry in coal tar dye wares. These colour factories afford a training to the chemist and chemical engineer which at present is hardly to be obtained in any other country or in any other branch of industry.

In short, the main thesis which should be pressed on the attention of all our public men and leaders of industry is that in regard to the safeguarding of our natural resources in *materia chemica* there is only one strategic chemical front, and we cannot fall behind in any particular branch of chemical trade without grave risks of losing ground in all the correlated industries.

Owing to the wide geographical distribution of the community of nations known as the British Empire, these countries exhibit within their boundaries striking diversities of geological structure with a varied assortment of mineral deposits. The exploitation of these mineral resources, so far as it has progressed, shows that the British Empire has a very generous endowment of the common and precious metals. The possession of this mineral wealth involves us, however, in the grave responsibility of utilising these hidden treasures to the best advantage. We must give a faithful account of our stewardship, otherwise sooner or later the task will be undertaken by others.

A comprehensive study of inorganic or

mineral chemistry shows us that each elementary type of matter is possessed of certain characteristic and unique properties which are not shared completely by another element, even when the two are closely related. Consequently the industrial employment of any element resolves itself ultimately into finding a use for one or more of its unique properties. The utilisation of such rare elements as neon, thorium and vanadium encourages the belief that ultimately some employment will be discovered for all the elements either free or in a state of combination.

Professor Morgan referred to the Empire's resources in the precious metals, gold and silver, and also to the light metals, aluminium, magnesium and beryllium, which are of special interest in the production of light alloys. Ultra-light alloys are now being produced by the Magnesium Co., Ltd., of Wolverhampton. The metals of the less common earths are utilised chiefly in the form of their compounds. Barium and strontium preparations are largely derived from British sources, and the world's requirements for thoria and ceria employed in the incandescent mantle industry, are largely supplied from the extensive Travancore deposits which will meet the demand for many years.

The favourable situation of the Empire in regard to the supply of tungsten minerals should place us in a premier position for manufacturing tungsten steel, but nevertheless, before the war, Germany controlled two-thirds of this production, the importation of German tungsten into this country having an annual value of £300,000. This unfavourable position, which existed up to July, 1915, was a contributory cause of the shortage of shell which jeopardised the military operations in the late war. He regarded the production of tungsten steel as one of the great triumphs of modern metallurgy. In the development of our mineral resources it is essential to take the long view. Systematic research is needed, even on chemical elements which have not hitherto received industrial application. Zirconium was cited as an instance of a metal which has so far been examined chiefly by German and American chemists, the English contribution to this branch of mineral chemistry being comparatively small. Cobalt is another example of a metal which merits increased attention, the annual production

being only of the order of 400 tons. The chief deposits are in Ontario, and Canadian chemists are becoming prominent as investigators of this element. Cobalt is a metal with a future, coming into use now as an alloy metal instead of being restricted, as it was until recently, to employment in combination as a pigment colouring material. Cobalt confers hardness and durability on aluminium. There is a world famine in regard to the valuable metals of the platinum group, owing to the partial failure of the Russian supply. These metals have been detected in many parts of the British Empire. Tasmania has furnished osmium and iridium, whereas the Sudbury nickel-copper ores of Ontario have yielded notable quantities of platinum and palladium.

Referring to magnesium, he pointed out that the metal, which has exceptional lightness, is permanent under ordinary atmospheric conditions, especially when free from impurities. Minute quantities of such foreign substances as alkalis or chlorides cause local granular corrosion. The metallurgy of magnesium depends on electrolytic processes, and considerable progress in this isolation has been made in the United States. The sudden drop in the number of producers and in the output is due to the competition of the German product. Germany controls a large portion of Austrian magnesite, and owing to the depreciated currency it can sell in any market in spite of import duties.

On the subject of beryllium, Professor Morgan had something interesting to say. Owing largely to the scarcity of beryllium, minerals, comparatively little headway has been made in the isolation of beryllium, although the physical constants of this metal show that it would be a valuable aid in the production of light alloys, providing that a sufficient supply of its minerals was forthcoming.

The commonest of these minerals, beryl, is an acidic silicate of beryllium and aluminium,  $3\text{BeO}$ ,  $\text{Al}_2\text{O}_3$ ,  $6\text{SiO}_2$ , occurring both in the old world and the new. A well known deposit exists at Limoges in France and considerable quantities have been noted in New Hampshire, where beryl crystals of enormous size up to  $2\frac{1}{2}$  tons occur native. Within the British Empire there is a small unexploited deposit in Glen Cullen, Co. Dublin. It is also found in the former German colony of S.W. Africa. Hitherto

only small quantities of beryllium metal have been produced. The first difficulty encountered in the metallurgy of beryllium is the separation of beryllium from alumina.

Beryl is an acidic felspar like orthoclase, and accordingly it is not appreciably attacked by the common mineral acids, hydrochloric, nitric and sulphuric acids. It is opened up, however, by fusion with caustic alkali, this reagent forming alkali silicate and yielding a mixture of alumina and beryllium carbonate. Subsequent treatment with dilute sulphuric acid precipitates silica. The filtrate contains beryllium and aluminium sulphate, and if the alkali used in the fusion contained potash, a good deal of aluminium sulphate crystallises in the form of potash alum and is thus separated. The beryllium remaining in solution as the more soluble sulphate is separated partially from the remaining aluminium by taking advantage of its solubility in ammonium carbonate, this reagent precipitating aluminium hydroxide. By diluting and boiling the solution, hydrated beryllia is precipitated and subsequently converted into the basic acetate,  $\text{Be}_4\text{O}(\text{CH}_3\text{CO}_2)_6$ , a co-ordination compound of considerable stability which, although only sparingly soluble in water, has the remarkable property of dissolving in such organic solvents as acetone, chloroform, benzene, etc. This beryllium derivative has a definite melting point, and when pure can be sublimed without decomposition. These singular characteristics render it useful in the final separation of beryllia from alumina.

Two other processes have been tried with good results, in Birmingham, by Mr. T. J. Hedley. These methods are based on the use of fluorides. In one process beryl is heated with hydrogen fluoride and ammonium fluoride until the silicon is volatilised and the residue contains the fluorides of beryllium, aluminium and iron. The second procedure, a French process, which obviates the use of poisonous hydrofluoric acid, consists in heating the finally powdered mineral with sodium silicofluoride. The product, on lixiviation with water, gives a solution containing sodium beryllium fluoride only, the other constituents remaining as sparingly soluble products. Whatever process was employed, it was found that the final purification is best effected through the basic acetate.

We are still only on the threshold of the metallurgy of beryllium. The purified acetate must be converted into oxide and fluoride when, by an electrolytic process akin to that employed for aluminium, the metallic beryllium is isolated. Even a moderate supply of beryllium or its alloys with copper and other metals would be an aid in aeroplane and airship construction. Beryllium, although a rare metal, is well worthy of the serious consideration of chemists and metallurgists.

Aluminium is the only fairly plentiful metal of the light metal group; some of the others, such as scandium, gallium, indium and thallium being excessively rare. Yttrium and lanthanum belong to the metals of the rare earths, comprising some 18 elements, of which certainly two have met with industrial application. These are thorium and cerium, both of which are derived from the mineral monazite, a phosphate containing several other metals of the rare earth series.

Having regard to the world's production in recent years, we should be in a premier position in regard to the production of incandescent mantles, the manufacture of which utilises the thoria and a small proportion of the ceria. Until the war, however, the manufacture of these mantles was largely a German and Austrian monopoly. The Travancore deposits were entirely in the hands of German agents, and all the mineral obtained was exported from India to Germany. During the war these enemy interests were eliminated and the industry placed on a satisfactory basis under control of British capital. These Travancore deposits are very extensive. They are the chief source of thoria, and will suffice to meet the world's requirements for many years. As by-products from the monazite concentrates, ilmenite (ferrous titanate) and zircon (zirconium silicate) are obtained. Both are separated from monazite by electromagnetic treatment. These by-products, which contain respectively titanium and zirconium, may come to have an economic value. The monazite exported from India in 1918 was 2,117 tons, valued at £58,820.

Although Germany is now obliged to purchase monazite from external sources, her activities in these markets show that the trade in thorium nitrate and incandescent mantles is very prosperous. During 1921 the output of incandescent mantles in Germany was 2,000,000 gross. The imports of incandescent mantles from Germany into

England in 1921 were 63,756 gross, or nearly three times the 21,359 gross imported in 1920. The value of the larger import was £111,917. In 1922, evidence given before the Committee appointed under Part 2 of the Safeguarding of Industries Act showed that of four thorium nitrate factories in the United Kingdom three were closed and one was working half time. The sales in Great Britain of British made incandescent mantles was 444,000 gross in 1920, but only 280,000 gross in 1921. A certain degree of support is afforded to the British industry under the Safeguarding of Industries Act, but a repeal of this measure would expose the newly created industry to the full force of German competition. This adverse factor is effective largely because of the depreciated value of German currency and the great difference between the internal and external value of the mark.

Titanium in the form of its oxide (rutile), or as the ferrous compound, ilmenite,  $\text{FeO}\cdot\text{TiO}_2$ , is widely diffused, and is among the more plentiful elements of the earth's crust. There is as yet no commercial method for producing elemental titanium. Difficulties arise owing to the chemical activity of the element and its high melting point (about  $1,800^\circ\text{C}$ ). The most important use of titanium lies in the production of ferrotitanium alloys. There are two of these, one containing carbon (0.8 per cent.) and the other free from this element. They contain respectively 15 and 25 per cent. of titanium. These alloys are used as deoxidizers, oxygen and nitrogen scavengers, and not as alloying materials. About 0.1 per cent. of titanium in the form of the Fe-C-Ti alloy is added to the steel as the last addition before pouring, and ten minutes are allowed to complete the action of the titanium.

Before the war there were 15 manufacturers of titanium alloys in Germany, 3 in Great Britain, 2 in France, and several in Sweden and Switzerland. Titania,  $\text{TiO}_2$ , is used in pigments; titanium white ( $\text{TiO}_2$  25% +  $\text{BaSO}_4$  75%). A good workable glass may contain titania replacing silica. A batch is given as containing

$\text{SiO}_2$	24-69 parts	$\text{Na}_2\text{CO}_3$	29 parts.
$\text{TiO}_2$	15-45	„ Lime	7 „
Borax	10	„	

Titania was utilised long before the war as an alternative refractory material to silica in the construction of crucibles. Like silica, it withstands sudden changes of

temperature without fracture, and being less basic it is less readily corroded by the basic metallic oxides used in gravimetric analysis.

Zirconium and its compounds are a worthy subject of chemical research.

Zirconia, which has a high melting point and low conductivity for heat, possesses a low coefficient of expansion, and withstands sudden changes of temperature. It is inactive towards most chemicals, and is scarcely attacked by strong acids, alkaline fusion mixture, or the ordinary fluxes and slags.

These properties point to the value of zirconia as a refractory material. It has been employed in making crucibles, muffles and combustion tubes which are gas-tight up to 1,000°. Zirconia crucibles have been used to melt pure iron, platinum, and tungsten alloys. Zirconia linings for the hearths of steel furnaces are very durable. It is also used to produce opacity in glasses and glazes. In medicine it has been substituted

for bismuth nitrate as a means of taking X-ray observations of the alimentary canal.

In this connection, Professor Morgan mentioned that two Danish chemists claimed to have discovered a new element in the zirconium minerals.\*

The Professor thought he had said sufficient to show that there was sufficient work to be done by all chemical students from the Birmingham and other English Universities. They cordially welcomed among them Mr. Pilcher, of the Institute of Chemistry, who is a good friend of chemists, and has done much to diminish unemployment among chemical graduates.

"Although chemical industry is temporarily under a cloud for various reasons," he added, "the outlook is not bad for the adequately trained chemist."

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\* Dr. A. Scott has also announced the isolation of an oxide of a new element from a similar source.

#### NOTES ON THE ACTIVE PRINCIPLES OF SOME SOUTH AFRICAN PLANTS.

By CHARLES F. JURITZ, M.A., D.Sc.,  
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(Continued from Page 70.)

#### III.—MAFEURA BEAN (*TRICHILIA EMETICA* VAHL):

This constitutes the seed of the Cape Mahogany (*Dutch-Essenhout*; *Kaffir-um-Kuhlu*), one of the most magnificent ever-

green trees in the forests of Pondoland, growing to a height of 80 feet, with a leafy canopy some 50 feet in diameter. The seed of this tree has of late years acquired some importance as a source of oil for soap making, and attempts have been made to utilise the cake after expression of the oil in a manner similar to that adopted for other oil cakes; that is to say, both for feeding purposes and as a fertiliser. The following analyses of this cake have been made in the laboratories of the Division of Chemistry, No. 1 at Cape Town, Nos. 2, 3 and 4 at Pretoria:

	No. 1.	No. 2	No. 3.	No. 4.
Moisture	11.98			
Ash	14.14			
Protein	22.93			
Oil	10.91	17.12	25.36	29.79
Fibre	9.66			
Nitrogen-free extract	30.38			
Nitrogen	3.67	3.93	3.51	3.00
Phosphoric oxide	1.11	1.17	0.63	0.57
Potash	1.84	2.79	2.19	2.14

From a fertilising point of view the article is not of very high grade, but it may be worth applying to hungry soils, poor in humus, and therefore, incidentally lacking in nitrogen. As a fertiliser it would not be profitable to transport it any distance, and it, moreover, possesses certain defects as a fertiliser inherent in its high oil content.

The poisonous nature of the seed is not as definitely settled as it might be. Dr. Marloth observed<sup>16</sup> regarding the genus *Trichilia*, "The seeds contain much oil: that of *T. emetica* is edible, while the oil of *T. Dregei* is employed by the natives only for greasing their bodies." Of course, it is quite possible that the oil may be edible while other constituents of the bean may be poisonous. Dr. Marchand, in his article on "Fertilisers" in the July, 1918, issue of the *South African Journal of Industries*, remarks that "the cake left after the expression of the oil is useless as a stock food, as it contains a poisonous principle," and he quotes an investigation by Mr. J. S. Jamieson, F.I.C., on the subject.<sup>17</sup> But Mr. Jamieson undertook the investigation not of the entire seed, but only of the bark and seed-oil of *T. emetica* (because the Rev. A. T. Bryant had described that bark as very poisonous), and stated in his opening paragraph that the "absence of toxic symptoms on administering it to guinea pigs upholds the view that it is not poisonous." Mr. Jamieson also states that he mixed about 10 grams of the fat from the seeds with mealie meal and administered it to a guinea pig with no toxic effect or symptoms. "The bark of *T. emetica*," he says, "which is known to the Natal Kaffir as the *um-Khulu*, is used as a purgative medicine." From the bark he extracted a rather refractory resin, to the large proportions of which he ascribed the purgative action of the bark. Mr. Jamieson's paper contains nothing whatever to warrant the inference that the seed either before or after extraction of the oil is in any way poisonous. On the other hand, I am informed by Mr. L. H. Hyman that the results of numerous experiments show the cake from *undecorticated* seeds to be extremely toxic, and to cause death invariably when fed to guinea pigs. Natives, he tells me, consume large

quantities of the *decorticated* kernel without any apparent harmful effect.

The Rev. A. T. Bryant, in his paper on Zulu medicine and medicine men,<sup>18</sup> includes *um-Khulu* (*T. emetica*) in a list of plants, of which he says "all of the following should be labelled at any rate as dangerous, many of them being most certainly fatally poisonous, and that, with some constitutions, even in minute quantities." "It must be recollected, however," he adds, "that every part of a plant is not always equally poisonous; that the noxious properties are not at all seasons equally great, and that they may at times be completely removed or neutralised by the method of medicinal preparation." (p. 12). Further on, he says, "The *i-Xolo* or *um-Khulu* (*T. emetica*) is a tree possessing very powerful medicinal properties, amongst others those of a purgative. A piece of the bark, of the length and breadth of two fingers, is pulverised and mixed into two teacupful of hot water as an enema, in which form this drug is usually administered." There is no reference by that author to any poisonous properties of the seed.

In my own paper on "South African Pharmacology,"† (†*Trans. S.A. Phil. Soc.*, Vol. XVI., p. 117) I referred to another species of *Trichilia* (*T. Dregeana* E. May). A Kaffir woman at Port St. John's died after using as an enema a decoction said to have been made from the latter plant, but the examination did not lead to any definite result.

Dr. T. R. Sim states<sup>19</sup> that "the seeds, which are striking objects, and may be gathered in bushels under old fruiting trees, are not eaten by birds or monkeys, and are not used, so far as I can learn, in Pondoland or Transkei," but he also quotes Oliver<sup>20</sup> as saying, "The oil and tallow obtained from the seeds, Dr. Kirk states, are valuable, and may be had in quantity. The oil is used in cookery."

From all the above it will be seen that the alleged poisonous character of the decorticated seed has no very definite scientific evidence to rest upon, although the shell or capsule thereof is apparently poisonous.

<sup>18</sup> *Annals of the Natal Museum*, Vol. II., Pt. I., 1909.

<sup>19</sup> "Forest Flora of Cape Colony," 1906, p. 161.

<sup>20</sup> "Flora of Tropical Africa."

<sup>16</sup> "The Chemistry of S.A. plants and plant products," p. 11.

<sup>17</sup> *Rept. S.A. Assoc. for Adv. of Science*, 1916, p. 496.

PROCEEDINGS AND NOTICES OF  
SOCIETIES.

THE ROYAL SOCIETY.

ORDINARY MEETING, JANUARY 25, 1923.

Sir Charles Sherrington, President,  
in the Chair.

The following papers were read, the summaries here printed having been supplied by the authors for use at the meeting:—

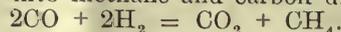
PROF. A. V. HILL, F.R.S. *The Potential Difference occurring in a Donnan Equilibrium and the Theory of Colloidal Behaviour.*

Loeb has shown experimentally that there is a potential difference between a colloidal solution of a protein and a crystalloid solution with which it is in equilibrium across a membrane, impermeable to the protein, but permeable to the other bodies involved. This P.D. varies in the same general manner as the osmotic pressure, the viscosity and the swelling, when the concentration of hydrogen ions or of salt is changed, and the manner of variation of the P.D. can be deduced, in general, from the theory of the Donnan equilibrium; hence it is concluded by Loeb that the Donnan equilibrium is the basis of the colloidal properties of protein solutions. While the probability of this conclusion is admitted, it is pointed out here that one of the chief arguments employed in its favour by Loeb is incorrect. Loeb shows that the P.D. observed experimentally agrees very exactly with that "calculated" from the difference in hydrogen ion concentration, also observed experimentally, and concludes that this supports his theory. As a matter of fact the equality he has observed is a necessary consequence of the manner in which his observations were made, and of general thermodynamical reasoning, and is independent of any theory of the mechanism by which the P.D. is produced.

E. F. ARMSTRONG, F.R.S., and T. P. HILDITCH. *A Study of Catalytic Actions at Solid Surfaces. X.—The Interaction of Carbon Monoxide and Hydrogen as conditioned by Nickel at relatively Low Temperatures. — A Practical Synthesis of Methane.*

Attempts to produce formaldehyde or methyl alcohol by passage of a mixture of carbon monoxide and hydrogen over nickel at temperatures 220-280° C. have been so far unsuccessful, but it was observed that under these conditions a mixture of equal

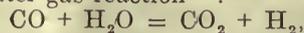
volumes of the two gases was largely transformed into methane and carbon dioxide:



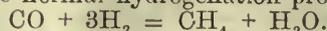
This action has hitherto escaped notice, although it affords the simplest and most economical means of producing methane in quantity, since a suitable gas mixture exists in ordinary commercial water-gas when the latter has been freed from catalyst poisons by removal of sulphur compounds.

The process is available for the preparation of pure methane, or for partial conversion of the original gas mixture, yielding a gas enriched to any desired degree in methane.

The action is at first sight anomalous, because it involves simultaneous oxidation and reduction of CO under entirely reducing conditions. The experimental data obtained are so far definitely against any intermediate formation of formaldehyde or methyl alcohol, but are compatible with a combination of what is usually known as the "water-gas reaction":—



with the normal hydrogenation process:—



Thus, of two volumes of water-gas (2CO + 2H<sub>2</sub>), one molecule of carbon monoxide and a molecule of water (either moisture present in the gases or catalyst, or formed by initial normal hydrogenation of some monoxide) interact and yield a molecule each of carbon dioxide and of hydrogen, the latter, with the balance of hydrogen present in the original gas, furnishing sufficient hydrogen for the normal hydrogenation of a second molecule of carbon monoxide.

J. HOLKER, D.Sc. *The Periodic Opacity of certain Colloids in progressively increasing Concentrations of Electrolytes.* Communicated by Prof. A. V. Hill, F.R.S.

In studying the effect of electrolytes on colloids it was found that, as the concentration of the electrolyte was increased, the opacity of the crystallo-colloidal solution varied in a periodic manner.

The method of testing the effect of common salt on the typical emulsoid colloid, serum, may be described. Into each of a series of test-tubes was pipetted 0.5 cc. of undiluted serum. To each tube was then added 2 cc. of solution of sodium chloride, which progressively increased in concentration in each successive tube. The tubes were then shaken and placed in a thermostat at 40° for four hours. At the end of that time the opacity of the solution was determined by a new method.



It was shown that the periodic phenomenon is a general one. It is given by colloids of both the emulsoid and suspensoid type, and by animal, vegetable, and mineral colloids. It is also given by certain mixtures of simple aqueous solutions of inorganic salts, e.g., by a "buffer" solution of phosphates to which are added progressively increasing concentrations of calcium chloride.

Emulsoid colloids tend to give many oscillations of low amplitude. Suspensoid colloids tend to give few oscillations of high amplitude.

For a given set of conditions the phenomenon tends to be more reproducible with emulsoid than with suspensoid colloids. When the degree of aggregation of a colloid is such that precipitation is imminent, reproducibility is markedly diminished.

The phenomenon is not an optical interference of the light scattered by colloidal particles, but is a definite oscillatory change in the physical condition of those particles.

E. K. RIDEAL and R. G. W. NORRISH. *The Photochemistry of Potassium Permanganate*. Part I.—*The Application of the Potentiometer to the Study of Photochemical Change*. Part II.—*On the Energetics of the Photo-decomposition of Potassium Permanganate*. Communicated by Sir William Pope, F.R.S.

The electrode potential of potassium permanganate undergoes a change (ca 0.25 volt) when illuminated with ultra-violet light from the mercury vapour lamp, and recovers slowly in the dark. This change is correlated with a photochemical decomposition of the permanganate, made apparent by the separation of a precipitate of the composition  $K_2O \cdot 2MnO_2$ , and the formation of a sol of  $MnO_2$ . Illumination establishes a photochemical stationary state, KOH being simultaneously produced by the decomposition, and removed by combination with the colloidal  $MnO_2$ . This involves an alteration of the  $P_h$  of the solution, which causes the electrode potential changes. From curves obtained the decomposition was shown to be monomolecular over the range of concentrations investigated, and from them it was impossible to calculate the velocity constant by two independent methods, the values obtained being in good agreement with that obtained by direct analysis of the decomposing solution.

The decomposition of acidified permanganate under identical conditions is of zero

order, the change in type of reaction being due to non-formation of colloid. The photosensitivity of mixtures of permanagante and oxalic acid is investigated, and the results embodied in a discussion of the mechanism of the decomposition of the permanganate ion. Attention is drawn to the use of the potentiometer for detecting and measuring photochemical change along the lines indicated in this paper.

The ultra-violet absorption spectrum of potassium permanganate is investigated, and the photoactive radiation shown to lie in this region. Evidence is given for considering the Hg line at 3128 AU. as the chief agent. The absorption of radiant energy was determined quantitatively; the result obtained is in agreement with the Einstein Law of Photochemical Equivalent, a result of special interest as the first instance of its application to solutions.

E. A. FISHER. *Some Moisture Relations of Colloids*. Part I.—*A Comparative Study of the Rates of Evaporation of Water from Wool, Sand, and Clay*. Communicated by Prof. A. Smithells, F.R.S.

A comparative study of the rates of evaporation of water, under comparable and rigidly controlled conditions, from a wool fabric, quartz sand, silty soil and heavy clay subsoil, has been carried out.

The curves obtained by plotting rates of evaporation against water contents are, in the cases dealt with, discontinuous and very different from the corresponding smooth vapour-pressure curves. Each portion of the rate curve can be expressed by a simple type of equation connecting rate of evaporation with water content. Various factors affecting the rate of evaporation are discussed in some detail.

The rate curves obtained are similar in type in the cases of wool (wholly colloidal with a cellular structure), quartz sand (wholly non-colloidal with a granular structure), silty soil (notoriously feeble in colloid properties), and heavy clay sub-soil (typically colloidal in behaviour). The conclusion is drawn that the forces holding the water are essentially similar in all four cases, and that colloid, merely as such, has no characteristic rate of evaporation curve. It is only when certain physico-chemical factors are operative, as in the case of gelatin, that the relatively simple type of evaporation curve is not followed.

The shrinkage of clay has a characteristic effect on the evaporation curve, which can be allowed for in the equation of rate. This

effect is entirely absent in wool, as in sand and silt, and it is concluded that the so-called shrinkage of wool on drying is really a deformation and not a volume shrinkage.

An attempt is made to explain the vapour-pressure relationships of wool on the basis of capillarity; the absorption of water by wool is attributed primarily to a filling up of fine pores of various shapes and sizes, and that the vapour pressures of wool-water systems are determined by the diameters of the pores that are full of water.

R. WHYTLAW-GRAY, J. B. SPEAKMAN, and J. H. P. CAMPBELL. *Smokes*. Part I.—*A Study of their Behaviour and a Method of Determining the Number of Particles they contain*. Communicated by Prof. A. Smithells, F.R.S.

A study has been undertaken of highly dispersed and dilute smokes, consisting of solid particles of ultra-microscopic size, with the object of discovering whether these systems present any analogy in behaviour to the solid-liquid systems of colloidal solutions.

The smokes were produced (a) by the arc discharge in air, (b) by volatilisation and condensation, (c) by chemical action. In each case highly dispersed systems of very minute particles could be obtained.

As a first line of attack, a method of counting with an ultra-microscope of the slit type the number of particles in a given volume has been worked out, and it has been found that, starting from the moment after dispersal, the life-history of a smoke falls into two main periods:—

- (a) An unstable period in which the number of particles diminishes rapidly with time.
- (b) A stable period in which the decrease in number is slow.

During the first period the increase in size is very marked, and it is shown that these changes are not due to evaporation, but to a process of aggregation, which produces complexes of different structure depending on the nature of the dispersed substance.

R. WHYTLAW-GRAY and J. B. SPEAKMAN. *Smokes*. Part II.—*A Method of Determining the Size of the Particles they contain*. Communicated by Prof. A. Smithells, F.R.S.

A filtration method has been devised which enables the concentration in weight of the suspended solid matter in these rapidly changing smokes to be determined with an accuracy of about 3 per cent.

A given volume of smoke (usually 1 litre) is filtered through small tubes containing asbestos, and the increase in weight is ascertained by means of a micro-balance sensitive to 0.0002 mgm. The process of filtration takes about five minutes. Curves have been obtained showing the variation in weight concentration of the smoke over periods of from 0 to 6 hours. Knowing the weight and the number of the particles in a given volume, the average mass of a smoke particle at different periods can be calculated and the growth followed in a quantitative manner. Assuming the density of the particle to be that of the substance in bulk, the average radius can be evaluated.

All the weight-concentration curves show an initial rise, and this fact, in conjunction with ultra-microscopic observations, renders it probable that all these clouds contain in the early stages a large number of invisible particles of a microscopic size.

R. C. RAY. *The Effect of Long Grinding on Quartz (Silver Sand)*. Communicated by Dr. W. M. Travers, F.R.S.

It is found that when quartz (silver sand) is ground for a long time, the density of the ground substance is lower than the one which has not been subjected to grinding. The fall of density shows that as much as 25.7 per cent. of the material is converted from the crystalline to the vitreous condition. This value agrees fairly with that arrived at from the determination of the molecular heats of solution.

#### PAPERS READ ON FEBRUARY 8, 1923.

PROF. L. BAIRSTOW, F.R.S., MISS M. B. CAVE, and MISS E. D. LANG. *The Resistance of a Cylinder moving in a Viscous Fluid*.

G. I. TAYLOR, F.R.S. *The Motion of Ellipsoidal Particles in a Viscous Fluid*.

L. F. RICHARDSON. *Theory of the Measurement of Wind by shooting Spheres upward*. Communicated by Dr. G. C. Simpson, F.R.S.

Papers read in title only.

PROF. W. E. DALBY, F.R.S. *Further Researches on the Strength of Materials*.

L. C. JACKSON and PROF. H. KAMERLINGH ONNES, For. Mem. R.S. *Investigations on the Paramagnetic Sulphates at Low Temperatures*.

L. C. JACKSON and PROF. H. KAMERLINGH ONNES, For. Mem. R.S. *Investigations on the Paramagnetism of Crystals at Low Temperatures*.

ERNEST WILSON. *On the Susceptibility of feebly Magnetic Bodies as affected by Tension.* Communicated by Prof. O. W. Richardson, F.R.S.

W. D. WOMERSLEY. *The Specific Heats of Air, Steam, and Carbon Dioxide.* Communicated by Sir Dugald Clerk, F.R.S.

## THE CHEMICAL SOCIETY.

### BYE-LAWS RELATING TO THE ELECTION OF PRESIDENT, OFFICERS, AND COUNCIL.

#### V.—Of the Constitution of the Council.

The Council shall consist of the President, not more than twelve Vice-Presidents, the Treasurer and Secretaries, and eighteen Ordinary Members. They shall conduct the business of the Society and may fill any casual vacancy in their number until the next Annual General Meeting. The President, Treasurer and the Secretaries shall be termed the officers of the Society.

An election to fill vacancies shall be held annually in manner hereinafter provided, and the result of the election shall be declared at the Annual General Meeting. The retiring members shall not be eligible for re-election until after the lapse of one year.

#### VI.—Of the Election of the Council.

In the month of January a list shall be prepared by the Council of the vacant places in the Council which fall due to be filled at the Annual General Meeting. This list shall be read at an Ordinary Scientific Meeting in January, and shall be published in the Proceedings. The Council shall at the same time and in the same manner intimate the names of the persons whom it proposes to nominate for the offices of President, Treasurer and Secretaries, should there be a vacancy in any of these offices.

A nomination for any vacancy among the officers, Vice-Presidents or Ordinary Members of Council may be made in writing signed by at least twenty Fellows, and must be received by the Secretaries at the Society's Rooms not later than the fourteenth day of February. Every nomination must relate to one vacant place only, and must be accompanied by a signed declaration by the nominee that he is willing to accept office if elected. Nominations may be made also by the Council.

The Council shall prepare the list of nominations for the vacant places, which shall include all candidates duly nomi-

nated. This list shall be read out by the Chairman at the first Ordinary Scientific Meeting in March, and shall be thereupon publicly suspended in the Society's Rooms, and if the number of nominations does not exceed the number of vacancies, the persons nominated shall be declared duly elected at the Annual General Meeting without any vote being taken.

If more candidates are nominated than there are vacant places, the Secretaries shall post to each Fellow usually resident in the United Kingdom a ballot paper containing a list of the vacancies for which there is a contest and of the candidates nominated therefor, distinguishing those who are nominated by the Council, and stating, in the case of candidates for the places of Ordinary Members of Council, how many are to be elected who are resident within fifty miles from Charing Cross, and how many beyond that radius, and the date by which the ballot papers must be received in order to be counted.

In the event of a ballot being required, two Fellows shall be appointed scrutators at the first Ordinary Scientific Meeting in March to assist in the subsequent counting of votes. In the event of either or both of these scrutators being unable to act, it shall be in the power of the President to appoint substitutes.

On some day previous to the Annual General Meeting the votes shall be counted by the scrutators, with the assistance of one of the Secretaries, and the scrutators, together with the Secretary, shall prepare and sign a report to the Council. A statement of the votes cast for each candidate shall be presented at the Annual General Meeting, and the Chairman shall declare the names of those duly elected.

In any case of equality of votes for two or more candidates, the Council shall decide which of the candidates shall be deemed elected.

#### XI.—Of the Ordinary Members of Council.

The term of office of Ordinary Members of Council shall be three years. If, before the expiry of this period, an Ordinary Member has been nominated for any other position on the Council, this nomination, if accepted, shall be deemed to create an additional vacancy in the list of Ordinary Members of Council.

The Ordinary Members shall be elected in such wise that nine shall be resident within a radius of fifty miles from Charing Cross and nine beyond such radius.

XX.—*Temporary Bye-Law.*

These Bye-Laws shall come into force on the first day of June, 1920.

Notwithstanding anything hereinbefore to the contrary, the Council which is in office when these Bye-Laws come into force shall be deemed to be the Council of the Chemical Society until the Annual General Meeting in March, 1921. It shall be the duty of this Council to make arrangements for the election of the Council for 1921-1922 in conformity with the foregoing Bye-Laws, and the terms of office of Members of Council elected at the first annual election after these Bye-Laws come into force shall be determined as follows:—

Of the twelve Vice-Presidents, two of each class shall retire at the end of one year and two of each class at the end of two years.

Of the eighteen Ordinary Members, three of each class shall retire at the end of one year and three of each class at the end of two years.

The Council shall determine, by arrangement or by ballot, which shall be the retiring members of each class for each year.

The Annual General Meeting of the Society for the election of officers and Council, and other business, will be held on Thursday, March 22, 1923, at 4 p.m.

## THE CHEMICAL SOCIETY.

*Burlington House,  
Piccadilly, London, W.1.*

Notice is hereby given that, in accordance with the Bye-Laws, the following vacant places in the Council fall due to be filled at the Annual General Meeting of the Society on the 22nd day of March, 1923:—

President, one vacancy.

Vice-Presidents who have filled the office of President, two vacancies.

Vice-Presidents who have not filled the office of President, three vacancies.

Treasurer, one vacancy.

Ordinary Members of Council—

(a) Town Members (*i.e.*, those living within a radius of 50 miles from London), three vacancies.

(b) Country Members (*i.e.*, those living beyond a radius of 50 miles from London), three vacancies.

The Council has nominated Professor W. P. Wynne to the office of President. It has also nominated Professor J. F. Thorpe to the office of Treasurer.

(In October last, the Council appointed Prof. J. F. Thorpe as Treasurer until the next Annual General Meeting, to fill the vacancy caused by the retirement of Dr. M. O. Forster. It also appointed Dr. J. T. Hewitt as Vice-President until the Annual General Meeting to fill the vacancy amongst the Vice-Presidents caused by Prof. J. F. Thorpe's appointment as Treasurer.)

Fellows are reminded that nominations for any of the above vacancies may be made in writing, signed by at least twenty Fellows, and must be received by the Secretaries at the Society's Rooms not later than the 14th day of February, 1923. Every nomination must relate to one vacant place only, and must be accompanied by a signed declaration by the nominee that he is willing to accept office if elected.

Forms of nomination can be obtained on application to the Assistant Secretary.

The names of the Members of Council who retire at the Annual General Meeting on the 22nd March, 1923, and who are ineligible for re-election to the same office until after the lapse of one year, are as follows:—

President: Sir James Walker.

Vice-Presidents who have filled the office of President: Professor H. E. Armstrong and Professor W. H. Perkin.

Vice-Presidents who have not filled the office of President: Professor F. S. Kipping and Professor S. Smiles.

Ordinary Members of Council—

(a) Town Members: Professor A. J. Allmand, Mr. F. H. Carr, and Professor J. M. Thomson.

(b) Country Members: Professor T. S. Patterson, Mr. W. Rintoul, and Professor R. Robinson.

JAMES C. PHILIP,

IRVINE MASSON,

*Secretaries.*

26th January, 1923.

## SOCIETY OF GLASS TECHNOLOGY.

Prof. W. E. S. Turner, D.Sc., President, presided at the meeting of the Society of Glass Technology, held in Sheffield, on Wednesday, January 17.

A very cordial welcome to the meeting was given to Mr. H. L. Dixon, of Pittsburgh, U.S.A., who was at present visiting Europe. He was, said Prof. Turner, well-known not only in America, but also in England and on the Continent. He had

built nearly all the glass furnaces in America.

The first paper presented to the meeting was by Dr. W. H. Hatfield, and entitled "Stainless Steel, with some Consideration of its Application to the Glass Industry." At the outset, Dr. Hatfield stated that he did not know sufficient of the glass industry to do anything more than suggest some directions in which stainless steel might be useful. He remarked that the most important property of stainless steel was its resistance to corrosion and to oxidation. The resistance to ordinary corrosion was not of much interest to glass technologists, but its resistance to oxidation at high temperatures was of considerable interest, especially from the fact that at high temperatures it scaled much less than ordinary steels. Stainless steel had such different properties from ordinary steel that it must be studied as an entirely different material from many points of view.

After demonstrating how nitric acid rapidly attacked ordinary steel but left stainless steel unaffected, Dr. Hatfield said that stainless steel could now be made direct into castings, while sheet steel, which was very malleable, could also be made. The making of sheet steel was a development of the last two years. Then, again, it could be drawn into tubes, so fine that hypodermic needles were now largely made from stainless tubes. Turbine blades had been successfully turned, and in this case the steel was brought into contact with steam at high temperatures. He showed pieces of turbine blades that had been in use eighteen months and still retained their special properties. These, he compared to ordinary nickel steel, which lost so much material that they had ceased to function properly. Practically all the turbine manufacturers had adopted stainless steel as being the most effective material for the manufacture of blades.

Stainless steel, he went on, was an alloy of iron and chromium. It contained from 12 to 14 per cent. of chromium. The carbon content varied a little with the different types of stainless steel, but for general purposes might be considered to be about 0.30 per cent., which was very similar to ordinary structural steel.

Dr. Hatfield showed by lantern slides the action of various corrosive and oxidising influences on stainless steel. They were able to make a stainless steel which would be impervious to sodium sulphate, though

some types of stainless steel were liable to be affected by continued contact with it. He showed micrographs illustrating the structure of various special steels, such as nichrome and tantiron. The former, he said, resisted oxidising influences and maintained its strength at high temperatures. Tantiron was not ductile, but relatively hard and brittle like cast iron.

With regard to the glass industry, he considered that stainless steels could be considered as alternatives for those now used, from two standpoints, which were the resistance to scaling and its strength at high temperatures. Stainless steel had a high tensile strength, equal to the best alloy steels, had a high fatigue range, and might be hardened and tempered. There were many directions in which the material might be useful, the most notable, in his opinion, being for parison and blow moulds. Many parts of feeder devices might be successfully produced in such material, as might also blowing irons, rolls, belt conveyers, lehr chain pins, and other things, including knives for cutting viscous glass. The ends of blowpipes might very well be made of stainless steel. Brushes which had to be made of wire could well be made of stainless steel.

Explaining recent developments in the use of this steel, Dr. Hatfield said that where a highly polished surface was needed, stainless steel was admirable for the purpose. Indeed, several firms were producing scientific mirrors from this material.

A discussion followed, in which there took part the President (Prof. W. E. S. Turner), Major V. F. Gloag, and Messrs. J. H. Davidson, W. C. Snowdon, R. Hemingway, and Guy Simpson.

Replying to the discussion, Dr. Hatfield said that the question of a good surface was answered by the manufacture of the mirrors he had referred to. He thought stainless steel would do very well in muffle lehrs. Stainless steel could be welded without any difficulty to stainless steel or ordinary steel, but a good deal depended on the skill of the smith employed. He thought that the moulds used in glassmaking were too heavy. Stainless steel could withstand the process of crushing and also ordinary wear and tear as well as most materials. He was not able to answer questions with regard to comparative costs, but the cost of stainless steel was something approaching the price of cheap high speed steel. It was a special steel, and not a cheap steel, but the cost

was not prohibitive. The expense was always justified when used in those industries where its special properties were an advantage over other materials.

The second paper was entitled "Some Measurements of the Viscosity of Glasses near their Annealing Points, and a critical Review of some recent literature on the Annealing of Glass," by S. English, M.Sc.

Mr. English showed that contrary to the general opinion, strain in glass could not always be detected by examining the glass in polarised light, and that the most sensitive position was that in which the direction of the strain in the glass was at  $45^\circ$  to the plane of polarisation of the light. In discussing strain viewers, the lecturer dealt with the defects in design of a strain viewer recently put on the market, and showed that with a strain viewer of this type it was very easy to obtain misleading indications of the presence of strain. Reviewing the statements made concerning the advantages accruing from the use of a selenite or quartz plate in connection with the analysing Nicol prism, it was shown that the claim made by one author that the selenite plate was more sensitive than plain crossed nicols was only true when a very poor source of light was used, and that a further claim made by another author to be able to distinguish between tension and compression stresses by the use of such a plate was entirely untrue.

Details of the measurements of the mobility of various types of glasses from the annealing temperatures through a range of  $150^\circ$  were given, and it was shown that the rate of change of mobility of the glasses at their annealing points was approximately constant, most of them requiring a rise of temperature of  $9^\circ$  to cause a doubling of the mobility. In some cases this temperature interval rose to as much as  $11^\circ$ . At temperatures of 100 or  $150^\circ$  above the annealing points the temperature interval required to double the mobility was generally rather longer than that required at the annealing points. Curves were shown indicating that the mobility of glasses is not a true logarithm's function of the temperature, and that a point of inflection in the curves will probably be found at temperatures rather higher than those included in the present range. It was also suggested that the well-known working properties of lead glasses and other soft glasses are determined more by the rate of radiation of heat than by rate of change of viscosity with temperature.

During the forenoon, by the courtesy of the directors, members had the privilege of visiting the works of Messrs. Thos. Firth & Sons, Ltd., Sheffield, where they saw various processes in the manufacture of stainless steel.

#### THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

##### PASS LIST: JANUARY EXAMINATIONS, 1923.

The following Associates have passed the examination for the Fellowship, in branch E, The Chemistry, including microscopy, of Food and Drugs:—

Two candidates were examined; both passed:

Hawley, John William, B.Sc. (Lond.).  
King, John.

The following candidates have passed the examination for the Associateship:—

Current Regulations: in General Chemistry:

Fifteen candidates were examined; seven passed:

Bender, Gustave William, University College, London.

Cattle, Alfred Philip, East London College.

Lomax, James, College of Technology, Manchester.

Madden, Frank Cox, University College, London.

McKean, John Brown, Paisley Technical College.

Powell, Cyril John, University College, Nottingham.

Reynolds, Thomas Edward Stewart, University College, London.

Regulations prior to 1920; in branch (a), Mineral Chemistry:—

Two candidates were examined; both passed:

Dallimore, Thomas Warwick, Chelsea Polytechnic.

Smith, William, University College, Nottingham.

Regulations prior to 1920; in branch (d), Organic Chemistry:—

Three candidates were examined; all passed:

Hansford, Mitchell Harold, Blackburn Technical College.

Tadman, Vernon Thorpe, University College, Nottingham.

Taylor, George, University College, Nottingham.

By Order of the Council,  
RICHARD B. PILCHER,  
*Registrar and Secretary.*

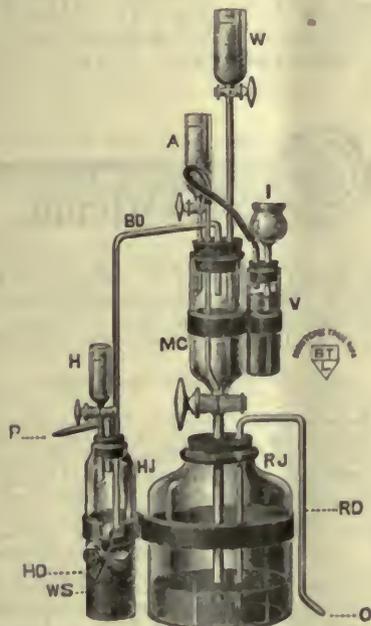
30, Russell Square, London, W.C.1.  
26th January, 1923.

## APPARATUS FOR THE RECOVERY OF BROMINE FROM SODIUM HYPOBROMITE.

By C. H. COLLINGS.

### Erratum.

P. 57, third line of third paragraph of first column: after the words "with the evolution of free Br," insert "a constant stream of air-bubbles."



The above illustration shows the apparatus used.

A, acid cup; W, waste-cup; H, soda sol. cup; HJ, hypobromite jar supports on WS, with delivery tap HD; MC, mixing-chamber; V, valve; I, air inlet; BD, bromine delivery tube; P, connection with aspirator or pump; RJ receives residuum from the operation in MC, and is emptied when full through RD at O.

### NOTICES OF BOOKS.

*Common Science*, by CARLETON W. WASHBURNE. Pp. XV. + 390. London: G. Bell & Sons, Ltd., Portugal Street, W.C. 1923. Price 4s. 6d.

A collection of answers to about 2,000 questions asked by children forms the foundation of this book.

These questions were selected from those asked by several hundred children in upper elementary grades. They were sorted and classified, and from them this course was constructed. The aim has been to select

simple and striking experiments and illustrations which will stimulate and maintain the children's interest in the subject.

The assumption that the scientific method can be taught to children by making them carry out uninteresting quantitative experiments in an effort to obtain results that correspond with those in a text-book can be considerably over-rated.

In the present volume, exercises are selected to illustrate the scientific principles of Gravitation, Molecular Attraction and Capillarity, Conservation of Energy, Heat, Radiant Heat and Light, Sound, Magnetism, Electricity, and Chemical Change and Chemical Action.

The volume is intended for young pupils who are studying elementary science, and should be useful to their instructors as well. J.G.F.D.

*Inorganic Chemistry*, by G. S. NEWTH, F.I.C., F.C.S. New and enlarged edition. Pp. XIII. + 772. London: Longmans, Green & Co., Paternoster Row, E.C. 1923. Price 8s.

The continued popularity of Newth's "Inorganic Chemistry," as evidenced by the constant issue of new editions, is not difficult to understand.

The book is just the type which appeals to those tutors who take students to the Matriculation and Intermediate Science stages.

It also appeals to students who are largely left to their own initiative to acquire an elementary knowledge of chemistry. This may be due in some measure to the fact that the author's aim has been to include descriptions of as many experiments as is consistent with the correct presentation of the theoretical matter.

It may be urged that the time has come for such a volume to be entirely re-written, but this does not necessarily apply to such a subject as elementary inorganic chemistry, especially if the important new developments are indicated.

This text-book will doubtless continue to be used in many schools and other institutes by those students for whom it is intended. J.G.F.D.

We have received from Messrs. Adam Hilger, Ltd., 75a, Camden Road, London, N.W.1, a copy of the second edition of their

*Optical Methods in Control and Research Laboratories*, by J. N. GOLDSMITH,

PH.D., M.Sc., F.I.C.; S. JUDD LEWIS, D.Sc., F.I.C., Ph.C.; and F. TWYMAN, F.Inst.P. Vol. I., pp. 56 + IV. + plates.

This volume, which costs 1s. 6d., or 1s. 8d. post free, deals with Spectrum Analysis, Absorption Spectra, Refractometry, and Polarimetry.

In the preface it is rightly pointed out that there is a tendency to lose sight of the deeper significance of physical properties when they are merely used for identification or other technical purposes. This tendency should be guarded against, and this has certainly been the policy of Messrs. Hilger, who have, from time to time, published valuable information concerning their instruments and the physico-chemical applications for which these may be employed.

In the present pamphlet, Section I. deals with Spectroscopy and analysis by Emission Spectra. The use of spectrum analysis has been very considerably extended during the last decade. Recent applications are very numerous, as is indicated by the references quoted. Section II. gives an account of Absorption Spectra and Spectro-photometry. Section III. is devoted to the Refractometer and its uses; and finally Section IV. deals with the Polarimeter. These sections are all followed by lists of references to the important and cognate publications on these subjects.

The pamphlet is thus seen to be of considerable value to the users of these physical instruments.

The Association of British Chemical Manufacturers, 166, Piccadilly, W.1, have sent us an *Official Directory of Members with a Classified list of their Manufactures*.

This directory should assist buyers of chemical products at home, in the colonies, and abroad. There are keys to the index in French, Spanish, Italian, Portuguese and German, which considerably enhance the utility of this directory, copies of which may be purchased at the offices of the Association, price 10s. 6d.

#### BOOKS RECEIVED.

*Seifen Und Erweissstoffe*, von MARTIN H. FISCHER unter Mitarbeit von George D. McLaughlin und Marian O. Hooker. Autorisierte Deutsche Ausgabe von DR. JOHANN MWTALA. Pp. 188. 1922. Dresden and Leipzig: Verlag von Theodor Steinkopff. 4s. 3d.

*A Text-Book of Inorganic Chemistry*, by

G. S. NEWTH, F.I.C., F.C.S. Pp. XIII. + 772. New and enlarged edition, 1923. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 8s.

*Outlines of Theoretical Chemistry*, by FREDERICK H. GETMAN, Ph.D. Pp. VIII. + 625. Third Edition, 1922. Messrs. Chapman & Hall, 11, Henrietta Street, Covent Garden, W.C.2. 18s. 6d. net.

*Questions and Problems in Chemistry*, by FLOYD L. DARROW. Pp. VII. + 177. 1923. Messrs. G. Bell & Sons, Ltd., York House, Portugal Street, W.C.2. 3s. 6d. net.



This list is specially compiled for the *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

#### Abstract Published this Week.

**Lead Sulphate.**—Patent No. 189160.—The invention is related to a process described in Specification 5299/15, granted to Messrs. J. Gitsham and H. R. Evershed, of 175, George St., Launceston, Tasmania, wherein sulphate, sulphite, and oxide of lead are obtained directly from the native sulphide by volatilising the latter in an electric furnace. The present invention aims at the production of a product free from sulphide, oxide, or unchanged sulphide. The finely crushed ore, which may have been previously concentrated, falls in regulated quantities from a feeding apparatus through the guide tubes on to the electrodes of the furnace. These are arranged in pairs, and are placed about nine inches above the floor of the furnace. About five feet above the arcs is an atmospheric intake communicating through a bifurcated flue with a fan chamber. A fan induces a current of air over the furnace shaft, and the fan chambers deliver into spray boxes, wherein the fumes are subjected to the action of water sprays delivered from a perforated pipe. A chimney assists the flow of air and fumes through the apparatus. The water containing the reaction products passes through launders into vats, where it may be warmed and agitated by steam pipes placed on the floor of each vat. The finely crushed sulphide falls on to the arcs, and is at once volatilised. The vapours rise up the furnace shaft into the current of air passing through the top of the furnace, and are then oxidised. The reaction products, having been delivered into the vats, they are agitated, and free acid may be added if necessary, to convert any sulphites or oxides present into sulphates. The agitation serves to float any sulphide that may have escaped volatilisation. This is skimmed off, dried, and retreated. The remaining liquor is neutralised with lime, and the sulphates finally allowed to settle, decanted, and dried for use as a pigment.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the official price of 1s. each.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3279.

## PASTEUR.

On Friday, February 2, a lecture was delivered, in French, under the auspices of the Alliance Française, by Doctor Pasteur Vallery-Radot, Médecin des Hôpitaux de Paris, in the rooms of the Royal Society, Burlington House. The Chairman was Sir Charles Sherrington, President of the Royal Society.

The lecturer was the grandson of the great scientist, and had lived with him in his youth; he stated that among all the homages paid to him on the occasion of the hundredth anniversary of his birth, none would be dearer to Pasteur than that England is paying him this month, because it is the land of Jenner and Lister, and because here he found his warmest partisans and some of his greatest friends.

Before Pasteur, medicine knew nothing of the cause of virulent illnesses; surgeons dared no longer operate, infection was the fear of maternity hospitals, the industries based on fermentation were powerless, herds were dying fast. In 40 years, Pasteur's genius changed all.

At 22 he already ranked as a great scientist, and from his study of crystals he was led to study fermentation, and whence he touched on the question of the "spontaneous generation of life."

He was a man who liked to obtain results, and he showed at once how the various industries could benefit by his studies on fermentation; he thus gave practical help to the wine, beer, dairy, vinegar, and bread industries; in a word, all that touches the necessities of life benefited through his work.

In 1865 he began the study of the plague which was ruining the silk industry, and succeeded in discovering the microbe which killed the silkworms. He then turned to help medicine and surgery. In 1877 he studied that disease, anthrax, which was killing cattle in such a quantity at this time; then fowl pestilence, or chicken cholera. He was dominated by the idea of saving humanity from epidemic, and was led to the discovery of vaccination by experiments carefully done. Microbes were thus transformed from an instrument of death into an instrument of preservation.

Pasteur studied rabies, and had there to fight hard against opposers who called him a murderer on account of his experiments on animals.

The work of Pasteur is, by its logical linking and its incalculable consequences, one of the most wonderful productions of man's genius; he had an extraordinary imagination, but he tempered it by the most strict experimentation. This is particularly exemplified by his researches upon disymmetry.

But if Pasteur was great by the mind, he was as great by the heart. Modesty was his great characteristic. To his father and mother he gave thanks for what life had given him. His work and his home life were closely linked because Madame Pasteur was his help in every moment.

He closely bound together the love of his country to his love for humanity. He often said that if Science had no country, the scientist should have one. His ideal was to see humanity lead to peace by the aid of science.

His grandson, a medical man by profession, is also a distinguished biologist; he has given special attention to the study of hypersensitiveness in *asthmas urticaire*, and its gradual or sudden cure by the swallowing before meals of a certain dose of peptone in tablets. He is also very deeply interested by the study of kidney troubles.

Mr. A. Chaston Chapman, President of the Institute of Chemistry, proposed the vote of thanks, and expressed the opinion that the thanks of the audience were due to the lecturer for his clear exposition of the achievements of his grandfather. As a chemist, he was specially interested in Pasteur's chemical achievements, by which he commenced his illustrious career.

The vote was seconded by Prof. Martin, and was carried with acclamation.

## THE RARE EARTHS AND THEIR METALS.

### II.—MODIFIED METHODS OF SEPARATION.

By JOHN MISSENDEN, B.Sc.

(Continued from Page 55.)

(a) Apart from periodic classification, which may only be considered for the evolution of new lines of research, the rare earth metals may, for all practical purposes, be divided into two groups:

- (a) The cerium group: Ce, La, Pr, Nd, (Di), Dp, Gd, Sm, etc. ;  
 (b) The yttrium group: Y, Yb, Sc, Lu, Ho, Er, Tr, Tm, etc.

The division of the metals depends upon the solubility in a saturated solution of potassium sulphate of the double potassium salt having the general formula,  $R_2(SO_4)_3 \cdot 3K_2SO_4$ , group (a) being precipitated.

(b) The main method of effecting a separation—specifically, in the case of splitting up a complex earth—is by the fractional precipitation with ammonia. The process, while standardised more or less, admits of some variation, and discrimination has been difficult. In simple analysis (*i.e.*, where an unknown earth has to be examined) the elimination of a certain amount of tedium seems barely possible. Where, however, a known earth is applied to the extraction of a specified oxide, by a careful examination of these variations, a really convenient process has been found, and may serve for general adoption in the laboratory. It is not put forward as a suitable process for separations on a considerable scale, however, for two reasons: firstly, ammonium salts are split up by praseodymia; and, secondly, the hydroxides are difficult to isolate.

(c) The fractionation referred to is based on Drossbach's explanation (*Ber. Deut. Chem. Ges.*, 1902, XXXV., 2826). He boiled the specimen earth in an ammonium salt, rendering soluble the more basic metals by displacing the ammonia. Precipitation, stage by stage, then takes place from the complex solution.

Where the earth contains large quantities of nitrates in natural form—this is the rule rather than the exception—it is as well to precipitate slowly by the usual method of ammonium-fractionisation. When the bulk of the natural nitrates have been dealt with, resort should be made to the ammonium-salt method of Drossbach. The most basic metals, *i.e.*, lanthanum, neodymium, praseodymium, gadolinium, and samarium, are left in the filtrate after the first process.

The continuation of the separation is engineered by repeating the fractionisation, this time dissolving the hydrides in *dilute* hydrochloric acid (not concentrated, as has been described in another work) of 0.125 strength, an excess of aniline being added. Ammonia is then admitted to the solution drop by drop, and a quite accurate fractionisation of those earths which are least soluble in aniline hydrochloride results.

(d) The double ammonium nitrates of the  $R(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$  order were submitted to a crystallisation process by Welsbach, who produced the two components of didymium by this process. The most soluble fractions were found to be the metals of the yttrium group. Drossbach (*Ber. Deut. Chem. Ges.*, 1902, XXXVIII., 2823) discovered a method whereby praseodymium and neodymium could be more speedily obtained, and it is a variation of the above. The difficulty of effecting a separation between lanthanum and didymium was overcome by Denis and Lemon (*Journ. Amer. Chem. Soc.*, 1915, XXXVII., 131), who resorted to fractional electrolysis. The separation of other earths will be found in a table of general reference at the end of this section.

(e) Bunsen devised the original method of separation by nitrate ignition. The principle of this process is briefly the fusion of a series of nitrates in complicated mixture, scandium having the lowest melting point of the yttrium group, and yttrium the highest. More energetic applications of heat cause decomposition of the nitrates in chemical mixture over the same range. Undecomposed matter is removed in each case by dissolving in water, and the precipitate freed by filtering.

(f) With regard to the content of the rare earths, Sir William Crookes, following a line of study parallel to that of Nilson and Krüss, arrived at a remarkable conclusion. Nilson and Krüss carefully examined the absorption spectra of the metallic nitrates obtained from a wide range of earthy specimens, and observed that the intensity of the absorption bands for different specimens was not identical. Crookes, examining the phosphorescent spectra, upheld this quite feasible opinion. The different phosphorescent spectra of the two separate basic fractions of yttria is a case in point, the two analyses each having their own characteristics.

(g) A complete separation, applicable to many of the rare earths, is described as under. It is a modification of S. J. Johnstone's method for the constitutional determination of monazite (*Journ. Soc. Chem. Ind.*, 1914, XXXIII., 55), incorporating investigations by Mosander, whose work in obtaining ceria is mentioned in I. (d) of this treatise.

The earth to be examined is completely dissolved in concentrated sulphuric acid, the ratio of the acid to the earth being as 3:1, and poured into 200 cc. (or even more)

of distilled water. The precipitate is taken away, and the process upon it repeated two or three times, the final washing taking place for several hours. The remaining liquid is poured into 500 cc. of weak ammonia solution, and, after half an hour, 250 cc. of hydrochloric acid solution (strength 0.1) is added slowly. 12 g. of ammonium oxalate (compare the works of Glaser) will commence precipitation. Here is the main deviation from Johnstone's method. When precipitation has stopped, the residue should be taken from the solution, reprecipitated and thoroughly cleansed in distilled water. 2 more g. of the oxalate added, and the next precipitated in a like manner; and so on, in 2 g. operations, until precipitation ceases. There will probably be six or seven grades of insolubles. (In the examination of pyrochlor by this method, nine separate precipitates were made. The first three were mixed together for the extraction of thorium, and the remainder put aside for further investigation. Originally, 10 grams of pyrochlor were used, and gave the results found on p. 54 of the *Chem. News*, Vol. CXXVI., very nearly.\*)

A part of these insolubles can be redissolved in hydrochloric acid (say 1 g. of insoluble to 35 cc. of a 0.1 solution after concentration treatment), and the whole made up to 250 cc. by the addition of water and sufficient ammonia to neutralise. 8 g. of sodium thiosulphate is then added to the former liquid at boiling-point, the whole being immediately cooled to 10° C. below the point of ebullition, and allowed to simmer for three days or more (the longer time causing the whole of the thorium to combine with the sulphate, thus eliminating further treatment with nitric acid afterwards).

The filtrate is now heated, and the water distilled off. The residue is dissolved in 20 cc. of hydrochloric acid, made up again to 250 cc., and oxalic precipitation again takes place to free the sulphate. This precipitate is treated precisely as explained by Johnstone from here to the end of the yttrium-earth extractions.

\* Pyrochlor was examined after the compilation of the table mentioned, and a note as to its composition will be added at the end of this section. A brief description of lanthano-tantalite will appear shortly. [Ref.: I. (h).]

In the division of the cerium-earths (i.e., ceria, lanthana, and didymia, etc.), the processes of Mosander are closely followed. Greater care is, however, exercised, in precipitation and purification. Lanthana and didymia are also precipitated as oxalates, and treated with nitric acid. The melting point of mixed lanthanum and didymium nitrate is about 428° C. when the mixture is in equal proportions. The molten liquid resolidifies in crystalline form, which, on boiling with 10 parts of water, throws down the basic salt. The soluble portion is fractionally separated, as has been previously described.

(h) The metal celtium has an oxide whose basic strength is between scandia and butecia, which is not as basic as neoytterbia (Blumenfeld and Urbain, *Compt. Rend.*, 1914, CLIX., 323).

(i) *References*:—

- Celtium: Urbain: (*Comptes Rend.*, 1911, CLII., 1b1).  
 Cerium: Schützenberger (*Compt. Rend.*, 1895, CXX., 663).  
 Brauner (*Chem. News*, 1895, LXXI., 283).  
 Nordenskiöld (*Pogg. Ann.*, 1861, CXIV., 612).  
 Decipium: Delafontaine (*Compt. Rend.*, 1878, LXXXVIII., 578).  
 Dysprosium: Cleve (*Journ. Chem. Soc.*, 1895, i., 476).  
 Erbium: Lecoq de Boisbaudran (see Dana).  
 Lecoq de Boisbaudran (*Compt. Rend.*, LXXXVIII., 323).  
 Gadolinium: Marignac (*Ann. Chim. Phys.*, 1880 [V.], XX., 535).  
 Holmium: S. I. Levy (*The Rare Earths*).  
 Lanthanum: Muthmann and Rölzig (*Ber. Deut. Chem. Ges.*, 1896, XXXI., 1718).  
 Drossbach (*ibid.*, 1902, XXXV., 2826).  
 Lutecium: Urbain (*Compt. Rend.*, 1907, CXLV., 759).  
 Welsbach (*Monatsh. Chem.*, 1913, XXXIV., 1713).  
 Neodymium: Baskerville and Stevenson (*Journ. Amer. Chem. Soc.*, 1904, XXVI., 54).  
 Praseodymium: Schéele (*Ber. Deut. Chem. Ges.*, 1899, XXXII., 409).  
 Meyer (*Zeitsch. anorg. Chem.*, 1904, XLI., 94).  
 Scandium: Nilson (*Ber. Deut. Chem. Ges.*, 1879, XII., 554).  
 (*ibid.*, 1880, XIII., 1439).

Samarium: Boisbaudran (*Compt. Rend.*, LXXXVIII., 323).

Terbium: Krüss (*Zeitsch. anorg. Chem.*, 1893, IV., 26).

Thulium: Welsbach (*Monatsh. Chem.*, 1913, XXXIV., 1713).

Ytterbium: Marignac (*Compt. Rend.*, 1878, LXXXVII., 578).

Yttrium: Cleve (*Compt. Rend.*, 1882, XCV., 1125).

(j) *Note on the Composition of Pyrochlor.*

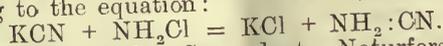
The specimen was obtained from Impilako in Finland, and bore much resemblance to that examined by Rammelsberg. Unfortunately, the total of the constituents only reached 98.72. The specimen contained 55 per cent. of niobium pentoxide, 10.52 per cent. of titanium dioxide, 8.1 per cent. of thorium dioxide, 6.37 per cent. of cerium sesquioxide. The amount of thorium dioxide noted on the table (p. 54) for this earth is 10.98 per cent., not 10.47.

(To be continued.)

### THE ACTION OF POTASSIUM CYANIDE ON MONOCHLORAMINE.

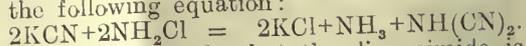
By W. F. SHORT, M.Sc., A.I.C.

The cyanamide required for an investigation of the interaction of its hydrochloride with phenolic substances (Short and Smith, T., 1922, CXXI., 1803) was not available from the usual sources. The interaction between potassium cyanide and monochloramine was examined in the hope that cyanamide would be produced according to the equation:

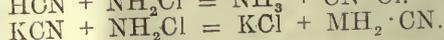
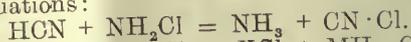


Raschig (*Verh. Ges. deut. Naturforsch. Aetze*, 1907, II., 120) states that monochloramine reacts with potassium cyanide in aqueous solution to produce cyanogen chloride and ammonia, but since Cloëz and Cannipzaro (*Ann.* 1851, LXXVIII., 229) have shown that these substances react to produce cyanamide, it was anticipated that by employing suitable experimental conditions cyanamide would be the main product. Instead of the anticipated result, the interaction led to the formation of dicyanimide, a new substance recently described by Franklin (*J. Amer. Chem. Soc.*, 1922, XLIV., 497), who prepared it by fusing sodamide with melon or by igniting sodium cyanide with mercuric cyanide.

The interaction of potassium cyanide and monochloramine takes place according to the following equation:



It seems probable that the dicyanimide is produced by the interaction of cyanogen chloride with cyanamide, these substances being first produced according to the equations:

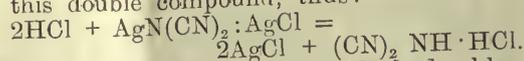


#### EXPERIMENTAL.

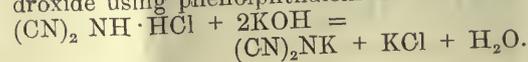
A solution of sodium hypochlorite containing approximately one gram molecule per litre was prepared by passing chlorine into an ice-cold solution of slightly more than two gram. molecules of caustic soda in a litre. To this solution, one equivalent of ammonia in semi-normal solution was slowly added by means of a capillary tube. One equivalent of potassium cyanide in concentrated solution was then added in a similar manner. The admixture of these reagents was carried out in a flask immersed in a freezing-mixture, the temperature being maintained below 5° C. After standing for five hours in an ice-chest, ammonia was added in sufficient quantity to retain in solution the silver cyanide produced on the subsequent addition of silver nitrate. A precipitate of glistening white crystals quite distinct from silver cyanide in appearance was produced. These crystals were collected, washed with a little water, and thoroughly dried in air. They darkened superficially on exposure to sunlight. Strong ignition produced a mixture of silver and silver chloride.

0.2015 gram left a residue of 0.1595 grams on ignition.  $\rightarrow (\text{AgN}(\text{CN})_2 \cdot \text{AgCl}) \rightarrow \text{Ag} + \text{AgCl}$  requires 0.2015 gram  $\rightarrow$  0.1596 gram). The residue, after treatment with nitric and hydrochloric acids weighed 0.1816 gram, whence  $\text{Ag} = 67.82$  per cent. ( $\text{AgN}(\text{CN})_2 \cdot \text{AgCl}$  requires  $\text{Ag} = 68.01$  per cent.). A determination of the nitrogen content by Kjeldahl's method gave  $\text{N} = 13.0$  per cent. ( $\text{AgN}(\text{CN})_2 \cdot \text{AgCl}$  requires  $\text{N} = 13.25$  per cent.).

Hydrogen chloride in ether decomposed this double compound, thus:



It was found that dicyanimide hydrochloride could be titrated with potassium hydroxide using phenolphthalein as indicator:



Biuret was produced by warming the hydrochloride with water. Cold hydrochloric acid converted the silver compound into cyanocarbamide,  $\text{NH}_2\text{:CO}\cdot\text{NH}\cdot\text{CN}$ , characterised by its copper salt. By treating the silver compound in aqueous suspension with hydrogen sulphide, removing the silver sulphide and concentrating the solution in vacuo, a jelly-like mass separated out. This appeared to consist for the greater part of an insoluble amorphous polymer of dicyanimide. On neutralising a dilute aqueous solution of dicyanimide with caustic soda and adding silver nitrate, a bulky white precipitate of the true silver derivative,  $\text{AgN}(\text{CN})_2$ , is obtained.

I have to thank Mr. R. Gardner, B.Sc., for assistance in carrying out the preliminary experimental work.

*Chemical Laboratories,  
University College,  
Auckland, N.Z.*

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL SOCIETY.

THURSDAY, FEBRUARY 1, 1923, AT 4.30 P.M.

The following papers were read:—

PROF. O. W. RICHARDSON, F.R.S. *The Magnitude of the Gyromagnetic Ratio.*

This note discusses various possibilities as to why this ratio has the value  $m/e$  instead of  $2m/e$ , the value calculated on the turning electron orbit theory of magnetism of the Langevin type, and suggests that the discrepancy is due to the rotation of the atomic nucleus. In the case of iron it appears that the effective electron orbits possess altogether two quanta of angular momentum per atom and the nucleus a single quantum of angular momentum on this view.

SIR RICHARD PAGET, BART. *The Product of Artificial Vowel Sounds.* Communicated by Sir William Bragg, F.R.S.

Experiments were made with plasticene resonators to imitate resonances heard by the writer in his own voice when breathing various English sounds. The first models were made in rough imitation of the oral cavity, and were found to give two double resonances.

Experiments were made with these models to ascertain the effects of various

alterations of form on the natural resonances of the model when tapped or blown through. The models were then tuned by appropriate alterations of form to give resonances similar to those heard in  $\nu$  (earth) and  $\alpha$  (calm) in the writer's voice. They then gave recognisable breathed vowel sounds when blown through a small orifice at the back.

An artificial larynx was made by means of a rubber strip laid edge-wise across a flattened tube, and, when blown through this larynx, the models gave recognisable voiced vowels.

Further experiments indicated that the oral cavity behaves in every case as two Helmholtz resonators in series, and the remaining vowel sounds were reproduced by forming two separate resonators joined together in series, and made of such capacity and size of orifices as to allow for mutual reaction of resonators on their respective resonant pitch.

In one case the vowel sound  $u$  (who) was apparently produced by a single resonator when blown by mouth through an artificial larynx. It was found that the vowel sound was due to the fact that the mouth cavity acted as a second resonator, i.e., that vowels may be produced by two resonators in series with a larynx between them. Certain vowel sounds in the mouth can be changed into others by adding a resonant capacity on to the mouth.

With a single cylindrical resonator, and with an ovoid resonator, it was found that when blown through by means of a small orifice at the back two or more resonances were given, some bore correct pitch relation to one another to give certain vowel sounds, i.e., a single tubular resonator may act as two resonators in series.

Two resonators in parallel, blown by means of a single larynx with a bifurcated passage, produced vowel sounds indistinguishable from resonators in series.

F. SIMEON. *The Carbon Arc Spectrum in the Extreme Ultra-Violet.* Communicated by Prof. A. W. Porter, F.R.S.

The results of this investigation may be stated as follows:—

(1) The arc-spectrum of carbon has been shown to give lines in the Lyman region at 1194, 945, 858, 687, 651, 640, 599 and 595, which have not been previously observed, and which correspond with prominent lines in the "hot-spark" spectrum studied by Millikan.

(2) Groups of lines have been found at 1657, 1560, 1335, 1329, 1260, 1194, 1175, 1036 and 651, of which those at 1329, 1260, 1194, 1036 and 651 do not seem to have been observed by any other worker, and that at 1657 has not been completely resolved heretofore.

(3) A new determination of wave-length has been made of the prominent lines in the carbon arc-spectrum.

PAPERS READ IN TITLE ONLY.

PROF. J. JOLY, F.R.S. *Pleochroic Haloes of Various Geological Ages.*

PROF. H. A. WILSON, F.R.S. *The Motion of Electrons in Gases.*

H. HARTRIDGE. *The Coincidence Method for the Wave-length Measurement of Absorption Bands.* Communicated by Prof. J. N. Langley, F.R.S.

(1) Measurements of the absorption bands of pigments by means of the ordinary spectroscope are found to be inaccurate because of the breadth of the bands and the indefiniteness of their margins.

(2) The adjustment of two similar absorption bands into coincidence is found to be effected with considerable accuracy. If then a spectroscope is designed in which two spectra are seen side by side on looking down the eyepiece, but reversed in direction with one another, the measurement of the mean wave-length of the absorption bands can be accurately carried out.

(3) The optical construction of the instrument is described in Section 3.

(4) The method of calibrating the micrometers of the spectroscope are described, and experimental values are given to show the accuracy obtained.

(5) The method for the quantitative estimation of pigments by the wave-length measurement of their absorption bands is described. The estimation is shown to depend on the movement of the bands which occurs when the concentration of one pigment changes.

(6) An example of the method is given, namely, the estimation of the percentage saturation of blood with CO gas by the measurement of the wave-length of the  $\alpha$ -absorption band. The accuracy of measurement is found to be approximately 0.7 A.U.

(7) Sources of error in the method are considered, and probable accuracy of measurement discussed. The probable error in setting two absorption bands into coincidence is found but little greater than that of setting two sharp black lines into

coincidence, or of making one line bisect the area between two others.

A. BERRY and LORNA M. SWAIN. *On the Steady Motion of a Cylinder through Infinite Viscous Fluid.* Communicated by H. W. Richmond, F.R.S.

This paper offers another partial solution of the problem of the motion produced by a cylinder, moving with uniform velocity through infinite viscous fluid. The so-called "inertia" terms are neglected and a solution is found which satisfies the boundary conditions on the cylinder and makes the velocity only logarithmically infinite in one direction at infinity. The relative velocity increases comparatively slowly with the distance from the cylinder and the solution may be expected to give a fairly good approximation to the motion at small distances from the cylinder.

In the first place the problem is solved by treating the elliptic cylinder as a limiting case of the ellipsoid. The solution, which in the case of the ellipsoid satisfies the boundary conditions and those at infinity, leads to a solution for the elliptic cylinder, which has the velocity at infinity logarithmically infinite in one direction. The plane laminae, both along and perpendicular to the stream, are considered as limiting cases, and further, the motion due to the circular cylinder is deduced as a special case of the elliptic cylinder.

Secondly, the solutions for the elliptic and circular cylinders are obtained directly from the equations of motion.

Finally, stream-lines, curves showing variation of velocity along stream-lines and curves of constant velocity are drawn for three limiting cases.

Some numerical results are given to show how slowly velocity does increase with distance from the cylinder. From these we are able to conclude that it is probable that the theory represents the facts fairly accurately for some considerable distance from the cylinder.

W. JEVON. *The Line Spectrum of Chlorine in the Ultra-Violet (Region  $\lambda$ 3354-2070 A).* Communicated by Prof. H. C. Plummer, F.R.S.

(1) Observations of the spectrum of the Cl discharge tube, which have not hitherto extended lower than  $\lambda$  3276 A (Eder and Valenta) have been continued as far as  $\lambda$  2070 A, by means of 10-foot grating and quartz-prism spectrographs.

(2) Wave-lengths and wave-numbers of nearly 200 newly observed Cl lines are re-

corded, together with the effects of variations of capacity on the intensities of more than 100.

(3) The constant differences ( $\Delta\nu$ ) 40.4, 67.1, 107.5, found by Paulson in pairs and triplets above  $\lambda$  3276 Å recur in a few pairs below that point. The significance of these separations in relation to the analysis of the spectrum, however, appears doubtful, since—

- (a) There is no apparent regularity in the intensities of the lines involved; and
- (b) No triplets having these separations been detected in the region under investigation.

M. H. EVANS and H. J. GEORGE. *Note on the Adsorption of Bases by Solids and the Thickness of the Adsorbed Layer.* Communicated by D. L. Chapman, F.R.S.

The authors have determined the amount of carbon dioxide adsorbed by unit surface of glass, at a pressure approximating to one-sixth of an atmosphere, and their results are in agreement with the assumption that the carbon dioxide is condensed on the surface of the glass in a liquid layer having a thickness equal to between five and six times the diameter of the molecule of the gas.

By combining this result with the published figures of Mülfarth (*Ann. d. Physik*, 1900, Vol. III., p. 328) on the relative adsorption by glass of the gases—acetylene, nitrous oxide, carbon dioxide, sulphur dioxide and ammonia—they deduce that at the same pressure these gases are adsorbed by the surface to such an extent that if they were present as liquid layers, the thickness of the layers would vary from (in the case of acetylene) three, to (in the case of ammonia) forty molecular diameters.

A direct determination of the degree of adsorption of  $\text{NH}_3$  made by them furnished a value which was of the same order as that calculated, as above, from Mülfarth's data.

The results are in disagreement with Langmuir's recent generalisation that the forces of attraction exerted by a surface do not extend to a distance greater than the diameter of one molecule.

PROF. L. BAIRSTOW, F.R.S., MISS B. M. CAVE, and MISS E. D. LANG. *The Resistance of a Cylinder moving in a Viscous Fluid.*

The equations of motion of a viscous fluid in the approximate form proposed by Oseen have been taken as a basis for new calculations on the resistance of cylinders. Calculations are given in the paper for the resistance of a circular cylinder, and for the

surface friction along a plane. In the case of the circular cylinder experimental information obtained at the N.P.L. is wholly suitable for the purposes of comparison with the present calculations. A resistance coefficient is found which is about 30 per cent. greater than that observed at the limit of the range of observation.

The calculations represent an extension of the solution by Lamb from values of Reynolds' number, *i.e.*,  $Ud/\nu$ , which are small (0.2 approx.) to values which may be as great as desired; the comparison with experiment is first made with  $Ud/\nu = 12$ . The only approximation, other than percentage accuracy of computation, is that represented by Oseen's form of the equations of motion; it is proposed to attempt the calculation with the full equations proposed by Stokes in order to account for the remaining 30 per cent. difference.

Calculations for the plane show singularities at the edges, but lead to a resistance which is in rough agreement with experiment. Exact comparison is not possible because the experiments were not carried out under conditions which sufficiently approach two-dimensional flow.

The analysis has been extended to cover the calculation of the resistance of a cylinder of any form for the same approximate differential equation. Whereas the circular cylinder and plane have been treated by analytical methods, it appears that graphical methods are required for the more general boundary form.

G. I. TAYLOR, F.R.S. *The Motion of Ellipsoidal Particles in a Viscous Fluid.*

The experiments here described were undertaken in order to test experimentally an unproved hypothesis recently introduced by Dr. G. B. Jeffery. The hypothesis was that ellipsoidal particles immersed in a moving viscous fluid would assume certain definite orientations in relation to the motion of the fluid. It was found that ellipsoidal particles made of aluminium and immersed in water glass do in fact take up the positions indicated by Dr. Jeffery, but they take a long time to get to those positions. During the time in which the particles are gradually approaching their final positions they oscillate in the way indicated in Dr. Jeffery's analysis.

PROF. W. E. DALBY, F.R.S. *Further Researches on the Strength of Materials.*

This paper describes my recent researches on the strength of materials, and is in continuation of papers published in *Proc. Roy.*

*Soc.*, A, vol. 86, and vol. 88, and in *Phil. Trans.*, A, vol. 221.

The papers describe first, a new apparatus by means of which an alternating load, push and pull, can be applied to a test piece in such a way that the curves of load and elastic extension are recorded photographically. Two records are shown, the one in which a test piece was broken down in tension, and the other in which a similar test piece was broken down in compression.

The immediate deduction from the records is that the yield in tension and compression is substantially the same, and that the modulus of elasticity is the same. But the point of greater interest is that alternating load is met by alternating response. When a load of either sign is removed the response is elastic, but imperfectly so. When a load is re-applied, but of opposite sign to the load removed, the response is mainly plastic. This alternating response to alternating loading is discussed in the light of the experiments of Ewing and Rosenhain and the recent researches of Carpenter.

The fact that Carpenter has found the elastic properties of an ordinary test piece reproduced in a test piece turned from a single crystal, definitely eliminates the amorphous network and allows the discussion to be based on the fact that elastic property resides mainly in the crystalline structure.

Many points requiring investigation are noted. A new instrument is then described by means of which an alternating torque and elastic twist are recorded photographically. A record is shown from which it is seen that alternating torque is also met by an alternating response in shear. Reference is then made to the possibility of predicting a practical fatigue limit from these diagrams.

LEWIS F. RICHARDSON. *Theory of the Measurement of Wind by Shooting Spheres Upward*. Communicated by Dr. G. C. Simpson, F.R.S.

During the last fifteen years a vast amount of information concerning upper wind has been obtained on occasions when the air was clear enough to allow a small rubber balloon to be seen through a theodolite. Some observations of wind above fog or low cloud have been made by tethered balloons carrying instruments, or by the method of sound ranging; but these observations are very scanty.

The new method, the theory of which is here described, is independent of visibility. A steel sphere, about the size of a pea or a cherry, is shot upwards from a gun, which is not rifled. The gun is inclined from the vertical towards the advancing air, and the tilt adjusted by trial until the returning sphere falls very close to the gun. The tilt is then some measure of a weighted average of the wind, in the region extending from the ground up to the maximum height attained. This height is found from the time of absence of the sphere, which is recorded by a stop-watch.

The observation of the tilt and time is repeated for greater and greater heights in succession. The result may be said to depend upon a set of weighted averages of wind up to successive heights; and the problem is to undo the averaging process, and so find the wind at each level. A condition of the problem is that the computation of the winds should not occupy the observer for more than about fifteen minutes.

Mathematically speaking, the problem involves a "linear integral equation of the first kind." This is solved approximately by transforming it into a moderate number of algebraic simultaneous equations. The error due to the finiteness of the number of these equations is studied by varying the number.

In the general part of the theory it is necessary to make an approximation which fails at the vertex of the trajectory. So for the sake of observations in which the important part of the path is near the vertex, there is given either a special and sufficiently correct theory or else a correction to the general theory.

ERNEST WILSON. *On the Susceptibility of Feebly Magnetic Bodies as affected by Tension*. Communicated by Prof. O. W. Richardson, F.R.S.

The experiments demonstrate that when magnetite is subjected to tensile stress ranging from about 50 to 130 kgm. per sq. cm. as a maximum, the susceptibility for a given value of the magnetic force at first increases and then decreases as the specific load continuously increases, and exhibits a reversal point as in iron. The magnetic force at which the percentage increase in permeability has a maximum value is less than the magnetic force at which maximum susceptibility occurs. The specimens



tested have widely different structural characteristics.

PAPERS READ IN TITLE ONLY.

L. C. JACKSON and PROF. H. KAMERLINGH ONNES, FOR. MEM. R.S. *Investigations on the Paramagnetic Sulphates at Low Temperatures.*

L. C. JACKSON and PROF. H. KAMERLINGH ONNES, FOR. MEM. R.S. *Investigations on the Paramagnetism of Crystals at Low Temperatures.*

W. D. WOMERSLEY. *The Specific Heats of Air, Steam, and Carbon Dioxide.* Communicated by Sir Dugald Clerk, F.R.S.

D. W. DYE. *The Valve-maintained Tuning Fork as a Precision Time Standard.* Communicated by Sir Joseph Petavel, F.R.S.

An investigation has been made of the variations in frequency of a valve-maintained tuning fork, when alterations were made in various quantities which might be expected to cause variations in frequency. The following quantities were varied:—

- (a) Temperature.
- (b) Anode voltage and filament brightness.
- (c) Capacity connected in parallel with grid and anode windings respectively.
- (d) Polarising magnetic field strength.
- (e) and (f) Energy taken from the system and the method of doing this.
- (g) Effective mass of different parts of the mounting and orientation of the fork and mounting in space.

In addition, various valves were tried and absolute measurements made of the frequency in terms of a standard clock, to a high order of accuracy.

The conclusions arrived at were as follows: The valve-maintained fork is steady in frequency to a degree beyond that required for most purposes. The most serious cause of variation of frequency is that due to temperature. The temperature must be kept constant to 0°.1 C. if accuracy to one part in a hundred thousand is required. By the use of a special steel known as "elinvar," having very small temperature coefficient of elasticity, it is probable that the variation of frequency with temperature could be reduced to one-tenth that of ordinary steel forks.

The other factors causing variation of frequency are not themselves variable without attention to an extent which would cause a variation of more than a very few parts in a hundred thousand. By suitably choosing the capacities and the anode volt-

age of batteries of + 10 per cent. will cause a change of only about one part in a million in frequency.

By observation of care in the adjustments of the factors affecting frequency, it is probable that sufficient accuracy would be attainable to observe diurnal variations in the rates of standard clocks, and perhaps in the value of "g."

[The abstracts are provided by the authors of papers, and are not to be communicated to any journal for publication until after the meeting.]

At the meeting on February 22, the Bakerian lecture will be delivered by G. I. Taylor, F.R.S., and C. F. Elam, on "The Distortion of an Aluminium Crystal during a Tensile Test."

ROYAL INSTITUTION OF GREAT BRITAIN.

ALBEMARLE STREET, PICCADILLY, W.1.

Saturday, February 17. — Sir ERNEST RUTHERFORD, LL.D., D.Sc., F.R.S., M.R.I., Prof. of Natural Philosophy, on *Atomic Projectiles and their Properties.* (Lecture I.)

THE CHEMICAL SOCIETY.

ORDINARY SCIENTIFIC MEETING, THURSDAY, FEBRUARY 15, 1923, AT 8 P.M.

The following papers were read:—

*Spinacene: Its Oxidation and decomposition.*—A. CHASTON CHAPMAN.

*Investigations on the dependence of rotatory power on chemical constitution. Part XIX.: The rotatory and refractive dispersion of d-γ-nonyl nitrite.*—R. H. PICKARD and H. HUNTER.

*Investigations on the dependence of rotatory power on chemical constitution. Part XX.: The rotatory dispersive powers of oxygen compounds containing the secondary octyl radicle.*—H. HUNTER.

PHYSICAL SOCIETY OF LONDON.

PROCEEDINGS AT THE MEETING HELD ON JANUARY 26, 1923, AT THE IMPERIAL COLLEGE OF SCIENCE.—ALEXANDER RUSSELL, M.A., D.Sc., IN THE CHAIR.

A paper on *A Supposed Relationship between Sunspot Frequency and the Potential*

*Gradient of Atmospheric Electricity* was read by Dr. C. CHREE, F.R.S.

ABSTRACT.

In a recent paper in *Terrestrial Magnetism*, Dr. L. A. Bauer draws the conclusion that both the range of the diurnal inequality of atmospheric electricity potential gradient and the mean value of the element for the year increase and diminish with sunspot frequency. This conclusion was based on observational data from the Ebro Observatory, Tortosa, Spain, between 1910 and 1920.

The present paper investigates the subject more mathematically, employing Kew electrical data from two periods of years, in addition to the Ebro data utilised by Dr. Bauer. Magnetic data from Kew Observatory for the same periods are similarly treated, so as to have parallel results from an element for which the sunspot relationship is generally admitted.

The results obtained are on the whole not incompatible with Dr. Bauer's conclusion, but they indicate that if a relationship of the kind supplied exists, the sunspot influence must be very much less in the case of atmospheric electricity than in that of terrestrial magnetism.

DISCUSSION.

Dr. A. Russell, in expressing the thanks of the meeting for an interesting and instructive paper, said that few realise the very high value of the potential gradient which normally characterises their physical environment, and which may have important biological effects, not only in connection with electro-culture, but also in human psychology. The "correlation coefficient" which Dr. Chree introduced was not familiar to all physicists, and appeared to be of very great interest as a test of the inter-relation of different phenomena.

A paper on *A Further Improvement in the Sprengel Pump*, by J. J. MANLEY, M.A., Research Fellow, Magdalen College, Oxford, was taken as read in the absence of the author.

ABSTRACT.

The paper relates to a further improvement in the pump described in the "Proceedings" of the Society, Vol. XXXIV., page 86, which is designed to avoid irregularities due to air skins on the inner surfaces of the apparatus. The present improvement consists in means for providing a mercury seal during periods when the

pump is out of use, whereby the formation of fresh air skins is prevented.

A paper on *Null Methods of Measurement of Power Factor and Effective Resistance in Alternate Current Circuits by the Quadrant Electrometer*, was read by D. OWEN, B.A., D.Sc., F.INST.P., Sir John Cass Technical Institute, London.

ABSTRACT.

Zero methods are proposed, and expressions derived, for the measurement of power factor and effective resistance of alternating current loads. The methods are extended to high tension circuits.

The effect of "electrical control" of the needle of the quadrant electrometer is discussed, and it is shown that the usual formula for the instrument is applicable only when the needle is maintained at its mechanical and electrical zero. The further advantages of null methods are emphasised.

Illustrative tests are recorded.

DISCUSSION.

Dr. E. H. Rayner congratulated the author on his valuable additions to the many uses of the Quadrant Electrometer. This wonderful instrument was invented over half a century ago by Lord Kelvin, but was still unsurpassed in its utility, being applicable to the accurate measurement of power, insulation, phase-angles, and many other quantities. The speaker took the opportunity to point out some details as to which care is necessary in the practical use of the Electrometer. (1) With high voltages the mechanical force on the needle is considerable and may bend it, leading to inconsistent results at low power factors. (2) Referring to Fig. 1 of the paper, the high resistance  $AO$  generally has an appreciable distributed capacity, with the result that the voltage across  $MO$  is not in phase with the current. If conditions permit, the easiest remedy is to take as much current along  $OA$  as possible; for instance, if the current in this branch be  $1/20$  ampere, the power factor in a common case would be 0.1 or 0.2 per cent., but on increasing the current to 1 ampere the phase lag might become negligible. A similar error has to be contended with where a step-down transformer is used, as shown in Fig. 5, and it must be remembered that for small phase-angles an error of a few minutes of arc may represent a large percentage error. (3) An extremely

important point when high voltages are applied to the needle is that the faces of the quadrants should be perfectly flat. To this end they should be ground on cast iron after they have been fixed in place.

Mr. G. L. Addenbrooke referred to his papers published in the *Electrician* in 1901 as relevant to some of the points raised by the author. He added that it is convenient to arrange a switch whereby the point *P*, Fig. 1 of the paper, may be connected at will to the point *O*. In this way the instrument may be converted into an ammeter. He had used deflectional methods because they permitted "seeing what was going on."

Dr. A. Russell congratulated the author on discovering so many theorems and applying them so usefully, and expressed appreciation of Dr. Rayner's helpful suggestions.

Capt. R. Dunsheath (communicated): This paper is very opportune at the present time, when so many investigators are seeking the best method of measuring dielectric losses, and is full of useful suggestions. I do not agree with the author, however, that it is desirable to eliminate both voltmeter and ammeter. His methods give power factor only, but a figure for actual watts lost is generally required. Also, due to the importance of the dependence of power factor and losses on voltage, it is usual to decide at the commencement of a test what voltage shall be adopted, and a voltmeter is essential. The ammeter is not so necessary as, having  $V$ ,  $N$ , and  $R$ , in formula (4), the value of the current follows at once. Proceeding in this manner  $\cos \phi$  is obtainable without the use of the cumbersome equation (6). It is, of course, necessary to switch one side of the voltmeter from *O* to *B*, but this is a simple matter.

I notice that Dr. Owen estimates the error of the figure obtained for phase angle on a  $1\mu F$  condenser at about 16 per cent. Much smaller condensers than this are usual in certain branches of industrial work, and it would be interesting to know the sensitivity of the instrument used, and what sort of accuracy might be expected if the method were applied to capacities of the order of  $0.01\mu F$ .

The author (in reply to the discussion): The remarks of Dr. Rayner will be valued by practical workers. The question of phase error in the shunt resistance, and methods of compensation have also been

treated by Orlich and Schultze. Mr. Adenbrooke's desire to follow what was going on by watching the deflection was, of course, quite natural. In the present methods this could always be done in the preliminary tests by slipping *P* into coincidence with *O* (see Fig. 1); for the final reading the zero balance would confer a distinct gain in accuracy. In reply to Capt. Dunsheath's inquiry, the sensitivity of the electrometer used in the tests quoted was such that with 100 volts on the needle and one-tenth of a volt across the quadrants the deflection was about 60 mm. at a metre scale-distance. This could have been multiplied three or four times possibly. Measurements on a  $0.01\mu F$  condenser could be conducted with much the same accuracy as those with  $1\mu F$ , since the resistance  $R$  could be increased in inverse proportion to the capacity.

A Demonstration of an Electro-Capillary Relay for Wired Wireless was given by MAJOR C. E. PRINCE, O.B.E.

The relay is intended for use with a calling device in connection with high-frequency currents acting as carrier waves for telephony over power-mains. The high-frequency current is rectified and passed through a thread of mercury which is contained in a capillary tube, and is in contact at each end with a quantity of acid, platinum wires by which the current enters and leaves, being immersed in the latter. The passage of the current causes the mercury thread to move, and it was suggested many years ago by Wheatstone that this thread might be made to close an electric circuit; but practical difficulties prevented the successful application of the idea. In the present invention the capillary tube is arranged horizontally on a beam which, as soon as the mercury moves, over-balances in consequence of the weight of the latter and closes the circuit of a call bell or lamp. To prevent the evaporation of the acid the cups containing it are connected by a further capillary tube which serves to equalise the pressure, and the tube in which the mercury thread lies is widened at its middle point to form a chamber for the reception of bubbles and other obstructions which may have got into the tube before sealing.

The circuit arrangements make provision for the restoration of the mercury to its original position whether the call be answered or not. In series with the thread and with a rectifier is arranged a condenser in which the charge that has passed round

the circuit is stored, and after the call this charge is sent through the mercury and acid in the reverse direction. The required discharge is effected by contacts which short-circuit the rectifier when the switch-hook is raised, but if the call be unanswered the same result is produced more slowly by a high-resistance leak.

The instrument will respond to currents of 4 or 5 or even 2 microamperes, and will function during long periods without attention. Its sensibility was demonstrated by passing through it the voice-current from the secondary of a microphone transformer, and subsequently the current from a single dry cell in series with the body of the demonstrator. If the leak resistance be small enough Morse signals will fail to effect a call in consequence of the leakage which takes place during the intervals between the signal elements, while a series of long dashes will nevertheless be effective and can be used as a call signal.

The cause of the movement of the mercury is obscure, and the phenomenon is of some interest to physicists. The total movement appears to be proportional to the coulombs which pass, so that the arrangement might be used as a quantity meter for small currents, such as voice currents.

#### NOTICE TO FELLOWS.

Fellows who have not already done so are kindly requested to forward information in regard to *change of address, or of title or degree*, not later than MARCH 1 next to

Mr. F. E. SMITH, F.R.S.,  
"Redcot," St. James's Avenue,  
Hampton Hill, Middlesex.

#### ABSTRACTS OF THE PROCEEDINGS OF THE GEOLOGICAL SOCIETY OF LONDON.

JANUARY 24, 1923, PROF. A. C. SEWARD,  
Sc.D., F.R.S., PRESIDENT, IN THE CHAIR.

The following communications were read:—

*On Reptilian Remains from the Karroo Beds of East Africa*, by SIDNEY HENRY HAUGHTON, B.A., D.Sc., F.G.S. (Read by Dr. A. Smith Woodward, F.R.S., Pres. L.S., F.G.S.)

Three specimens of a small fossil were found by Mr. F. P. Mennell, F.G.S., in black shale in the middle of Karroo Formation, near Tanga, on the coast of Tanganyika Territory. Two are well preserved, and

are now described in detail. They represent a new genus and species of aquatic reptile, in general appearance much like *Mesosaurus*, but differing in its shorter neck, thinner ribs, relatively larger and more massive fore-limb, the presence of a large rounded sternum, and of only four distal carpal and tarsal bones instead of five. It is perhaps more closely related to *Youngina*, and may be regarded as an aquatic adaptation of that type. If so, the shale at Tanga is approximately of the same age as the Middle Beaufort Beds of South Africa.

*Glacial Succession in the Thames Catchment-Basin*, by the REV. CHARLES OVERY, M.A., F.G.S.

This paper is intended to establish a definitive succession-grouping for high-level gravels of the Thames catchment-basin, analogous to that adopted for the valley-gravels proper. The necessity for this arises from the present confused system of nomenclature, and the lack of correlation between different areas. It is indispensable to the establishment of the Glacial Succession.

The Kennet Stages of H. J. Osborne White are dealt with, and an analysis is given of the Plateau-Gravels of Oxfordshire: the grading of these with reference to river-level, establishes a simple correlation with the Kennet Stages.

The author advocates the adoption of a norm series with effective nomenclature for the Berkshire-Oxfordshire area: namely, P<sub>350</sub>, P<sub>300</sub>, P<sub>265</sub>, P<sub>230</sub>, P<sub>210</sub>, P<sub>200</sub>, P<sub>135</sub>. If this norm series is represented in the Hampshire and London areas, succession-grouping, according to this scheme, possesses high significance.

Grading and analysis in the Hampshire and London areas result in the establishment of the norm series for the whole river-system. In this way light is thrown on such vexed questions as the age of the Goring Gap, the mode of description of the Plateau-Gravels, Glacial Succession in the Thames Basin, and, finally, on the bearing of the distribution of Drift constituents on the history of the Thames river-system.

The author claims to furnish definite evidence for the course of the pre-Pleistocene Thames, for the continuity of the Evenlode, Goring Gap, Henley Gorge, Colne-Lea divide, and Essex-coast system. He is able to correlate the deposition stages with recognised Glacial Epochs, and con-

cludes with deductions as to the age and succession of the implementiferous gravels of the Thames and its tributaries.

### BOROUGH POLYTECHNIC INSTITUTE.

#### DISTRIBUTION OF PRIZES BY THE ATTORNEY-GENERAL.

The Attorney-General, the Rt. Hon. Sir Douglas McGarel Hogg, P.C., K.C., M.P., distributed the prizes at the Borough Polytechnic on Friday, February 2. The Chairman of the Governors (Mr. J. Leonard Spicer) presided. In introducing the Attorney-General, Mr. Spicer referred to the pleasure it gave all those connected with the work of polytechnics that in Sir Douglas Hogg they welcomed one whose whole life had passed in the polytechnic atmosphere and tradition. Sir Douglas Hogg's father, Mr. Quintin Hogg, had been the founder of the Polytechnic in Regent Street, and Sir Douglas himself had, throughout his life, been associated with that Institute.

Sir Douglas Hogg, in his address, after referring to the great loss suffered through the death of Lord Kinnaird by all those interested in the youth of London, described the origin and aims of the great polytechnic movement which had taken shape in the formation 30 years ago of such institutes as the Borough Polytechnic. With regard to the work of the Institute, he said it was not their desire to turn out a number of half-fledged amateurs to compete with the men in the workshops, but by technical instruction to enable those in the workshops to make themselves more efficient and to make greater progress in the industry to which they belonged. He was sure that the policy which had actuated the Governors in supplementing the experience of the workshop by this technical instruction was a sound one, as was the policy of selecting teachers who themselves had knowledge of their industries.

It was very good to see that the women's side of the Borough Polytechnic was so strong. Some of the activities of the Borough Polytechnic were unique in this part of England; the School of Bakery and Confectionery had no parallel in the South-Eastern Counties, and the Department of Painters' Oils, Colours and Varnishes represented a highly specialised and very valuable piece of technological work. The Borough Polytechnic was to be congratulated

on the way in which it had enlisted the help of associations of employers, expert trade committees, trades unions, and associations of employers in order to keep its work closely related to the current needs of industry. In addition, however, to purely technical instruction, the social side of the Institute was a very strong one; it was concerned even more with the education of good citizens than with the production of expert craftsmen.

Principal Bispham, in his report, pointed out that both in quality and bulk the work of the session under review was a record one for the Institute, and an altogether worthy tribute to the former Principal, Mr. C. T. Millis, who had just retired.

Other speakers were Mr. F. A. Strauss, M.P., the Mayor of Southwark, Mr. D. Clifford Highton (Vice-Chairman of the Governors), Mr. P. M. Evans (Clerk of the Clothworkers' Company), and Mr. F. W. Mills (Chairman of the Students' Electoral Committee).

#### OBITUARY NOTES.

##### THE LATE MR. W. WOOLLEY, J.P., OF BLACKBURN.

Great regret has been caused at Blackburn through the death of Mr. W. Woolley, J.P., of the Bungalow, Meins Road, in that town, at the age of 58 years. He was the head of the firm, J. Woolley, Ltd., manufacturing chemists, and had been seriously ill for a few weeks. In the hope of bringing about an improvement in his condition, two transfusions of blood were resorted to. In each of these cases his sons volunteered to undergo the operation, the last being only a few hours before Mr. Woolley's death, when the required quantity of blood was given by a younger son, Mr. Harold Woolley, who is at the Agricultural College, Preston.

Mr. W. Woolley's early life was spent in Preston. All his life he was connected with the Wesleyan body, and he filled all offices open to laymen in the circuit. He had also worked for and held responsible positions in relation to the Blackburn Free Church Council, the Sunday School Union, and the Band of Hope Union. For six years he was a member of the Blackburn Town Council. In November, 1916, he was made a Justice of the Peace for the Borough of Blackburn. He has left a widow and three sons.

Professor William von Röntgen, the discoverer of X-rays, has died at Munich at the age of seventy-eight.

Though a German, he was educated in Holland and Switzerland, taking his doctor's degree at Zurich in 1869.

After holding minor appointments, he settled at Wurzburg as Professor of Physics in 1885, and later became director of the Physical Institute, Munich, a post he resigned four years ago on account of advancing age. He applied mathematics to practically every branch of physics, and while at Wurzburg he discovered the Röntgen rays, or, as he called them because of their character, the X-rays. That epoch-making discovery was the result of a series of experiments he conducted in 1895 on the phenomena resulting from the passage of electricity through the vacuum tubes invented by Sir William Crookes. The tube was enclosed in an opaque case, and Röntgen was astonished to find that certain radiations from the tube passed through the case and caused a fluorescent effect on objects outside.

With the caution of the true scientist, Röntgen was in no hurry to announce his discovery, but concentrated on a long series of confirmatory experiments. More than a year later he felt justified in making public his sensational discovery.

His other physical researches are of interest mainly to scientists, but the discovery of the X-rays has assured his name a permanent place in the roll of those men of science who have wrested secrets from nature of inestimable value to the world at large.

### GENERAL NOTES.

#### THE DETECTION AND ESTIMATION OF SMALL QUANTITIES OF ARSENIC.

JOINT MEETING OF THE SOCIETY OF PUBLIC ANALYSTS AND THE NOTTINGHAM SECTION OF THE SOCIETY OF CHEMICAL INDUSTRY.

For the first time in the history of the two Societies, a joint meeting of the Society of Public Analysts and of the Nottingham Section of the Society of Chemical Industry has been held. On January 17 more than 50 of the members of the Society of Public Analysts went to Nottingham to take part in the discussion on the methods of estimating arsenic, and were entertained at dinner by the local section prior to the discussion which took place in the Lecture

Theatre of Nottingham University before a crowded audience.

The chair was taken by Mr. Burford, Chairman of the Nottingham Section, and the discussion was opened by Mr. A. Chaston Chapman, F.R.S., who described his experience during the last 25 years with the zinc-acid process, and gave an outline of his procedure, more particularly in the use of cadmium to render the zinc sensitive.

He was followed by Mr. Wilkie, Secretary of the Nottingham section, who demonstrated the use of his electrolytic method of estimating arsenic, in which the reversibility of the reaction was prevented.

The next speaker was Dr. Monier-Williams, who showed an electrolytic Marsh apparatus modified from that in use in the Government Laboratory.

Major Trotman was of the opinion that the preliminary treatment of the material was the crucial point of the estimation. He advocated the calling of a conference to discuss the standardisation of methods of estimating arsenic.

Mr. H. Droop Richmond attributed the want of sensitiveness of the zinc in the zinc-acid method to the presence of iron, and Mr. J. Webster described an experiment indicating that the total amount of arsenic in a large organ, such as the liver, was correctly estimated by multiplying the amount found by a factor.

Mr. Jenson, Dr. Dyer, and Mr. Weaver also joined in the discussion, and Mr. P. A. Ellis Richards (President), and Mr. E. R. Bolton (Secretary) expressed the thanks of the Society of Public Analysts for the hospitality which had been shown to them by the Nottingham section.

#### ROYAL INSTITUTION.

On Tuesday, February 13, at 3 o'clock, Professor A. C. Pearson delivered the first of two lectures at the Royal Institution on "Greek Civilisation and To-day": (1) "The Beginnings of Science"; (2) "Progress in the Arts." On Thursday, February 15, Professor B. Melvill Jones began a course of two lectures on "Recent Experiments in Aerial Surveying," and on Saturday, February 17, Sir Ernest Rutherford will commence a course of six lectures on "Atomic Projectiles and their Properties." The Friday evening discourse on February 16 will be delivered by Professor A. V. Hill

on "Muscular Exercise," and on February 23 by Professor A. S. Eddington on "The Interior of a Star."

A General Meeting of the members of the Royal Institution was held on February 5, Sir James Crichton-Browne, Treasurer and Vice-President, in the chair. The deaths of Lord Kinnaird and the Hon. R. C. Parsons, members, and of Professor G. Lemoine and G. Lunge, honorary members of the Institution, were reported, and resolutions of condolence with the families were passed. The special thanks of the members were returned to Dr. Ernest Clarke, for his donation of £100 to the Fund for the Promotion of Experimental Research, and to Sir Humphry Rolleston for his gift of Sir Humphry Davy's honorary diplomas. Mr. and Mrs. Macnab were elected members.

#### IRISH CHEMISTRY STUDENTS AT BIRMINGHAM.

Recently the Senate and Council of the University of Birmingham received a request from the Royal College of Science, Dublin, to make provision at Birmingham University for eight senior students of chemistry who wish to do laboratory work, the commandeering of their alma mater by the Free State authorities having made it impossible for them to complete their studies in Ireland. The necessary arrangements were made for their reception, and all of them are now working under the supervision of the Dean of the Faculty of Science in the Chemical Department at the new University buildings at Edgbaston. From an academic point of view the hard necessity which has compelled these gentlemen to cross St. George's Channel is to be deplored, but Midlanders will feel some satisfaction in the thought that it was their university which was selected by those competent to judge when the question of transmigration was considered.

At a meeting of the Council of the Institution of Electrical Engineers, held on February 1, the following resolution was passed:—

"That in view of the present state of trade and employment, the Council request members who place, or who advise upon the placing of orders, to specify, as far as practicable, that the plant and material ordered shall be of British manufacture."

#### NOTICES OF BOOKS.

*Organic Chemistry, or the Chemistry of the Carbon Compounds*, by VICTOR VON RICHTER, edited by PROF. R. ANSCHUTZ and DR. H. MEERWEIN. Vol. III. *Heterocyclic Compounds*. Translated from the Eleventh German Edition by E. E. FOURNIER D'ALBE, D.Sc., A.R.C.Sc. Pp. XVIII. + 326. London: Kegan Paul, Trench Trubner & Co., Ltd. 1923. Price 25s. net.

The publication of this volume on the heterocyclic organic compounds completes the translation of the eleventh German edition of *Richter*, which appeared in 1912.

There is undoubtedly a demand for this translation—long overdue—but it is very regrettable that the important work accomplished by many eminent workers since 1912 is missing from the latest edition of this widely-consulted compilation. This is very noticeable, for instance, in the section on Vegetable Alkaloids, which is by no means up-to-date.

Another exasperating feature of this edition is that references to the original memoirs of authors outside Germany are to the *Chemisches Zentralblatt*. Authors' names are also seldom given. The same applied to Vol. II., reviewed in *The Chemical News* (1922, CXXIV., 226), April 21.

Thus, in the present volume, the reference on p. 89 to Moureu and Lazennee's synthesis of pyrazolone is C. 1906, II., 434. Pyman's researches on histidine and Lusk's work on amino-acids are quoted in the same manner. Examples of this kind could be further multiplied.

The intention in the original, evidently, was to assist German readers, but it would surely have been worth while to introduce French, English, American, and other original references in this translation.

Apart from these drawbacks the volume, which is well indexed, will serve a useful purpose until it is superseded by a subsequent edition. J.G.F.D.

*Seifen und Eiweissstoffe*, von DR. MARTIN H. FISCHER unter Mitarbeit von G. D. McLAUGHLIN und MARIAN O. HOOKER. Autorisierte Deutsche Ausgabe von DR. JOHANN MATULA. Pp. 188 + 37 plates. Dresden and Leipzig: Verlag von Theodor Steinkopff. 1922. Price 4s. 3d.

Dr. Matula's German translation of the

work of Dr. Fischer and his collaborators will bring to the notice of Central European scientists the researches and ideas of these American physical and biological chemists.

After an introduction on the preparation of soaps, the systems soap-water, soap-alcohol are considered, together with cases of colloidal soap solutions in non-aqueous solvents.

Then follows an account of colloidal phenomena in general, from which the author proceeds to the study of colloidal proteins, the behaviour of which he considers analogous.

The proteins and their derivatives have been investigated in this manner in order to arrive at a better understanding of their biological significance.

Part II. gives the author's version of the preparation of soaps from the standpoint of colloid chemistry, in which the hydration theory is supported.

In Part III. analogies are adduced between the behaviour of soaps and albuminates and organic tissues.

Part IV. is by way of a supplement, containing physico-chemical data of various series of acids of importance in soap-making.

So far as the reviewer is able to judge, the translation has been well done, and although the views expressed are not always those generally accepted and understood, this edition should be well received.

J.G.F.D.



THIS list is specially compiled for the *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

*Latest Patent Applications.*

901—Chemical & Metallurgical Corporation, Ltd.  
—Acid-resisting tanks, etc. Jan. 10.

- 1775—Phopal Produce Trust, Ltd.—Process for obtaining oxalic acid or its salts. Jan. 19.  
1674—Clayton Aniline Co., Ltd.—Treatment of  
836—Cowburn, A. W.—Production of concentrated sulphuric acid. Jan. 10.  
734—Roucka, E.—Apparatus for measuring and transmitting values of physical or chemical quantities. Jan. 9.  
1673—Alcock, H. E.—Manufacture of phosphoric acid. Jan. 18.  
1301—Frink, R. L.—Producing alumina and glass-making salts. Jan. 15.  
1666—Nobel, L. A.—Process for removing nitrogen from metal and alloys. Jan. 18.  
1630—Vautin, C. T. J.—Extraction of copper from its ores. Jan. 18.  
1787—V.L. Oil Processes, Ltd.—Treatment of mineral oils. Jan. 19.

*Specifications Published this Week.*

- 190733—Barton, G. V., and Lead Products Syndicate, Ltd.—Apparatus for the manufacture of lead oxide.  
190754—Foster, A. B.—Process of treating hydrocarbon oils and tars.  
190923—Linde Air Products Co.—Process and apparatus for the separation of gaseous mixtures.  
190961—Mueller, M. E.—Method of recovering hydrocyanic acid from gas.  
191117—Howland, A.—Analysis, synthesis, arrangement, and notation of colours, and apparatus thereof.  
191122—Abbott Laboratories.—Production of certain esters of aromatic acids.  
191129—Adeltanado, L.—Manufacture of superphosphates and manure.  
191167—Turner, W. L.—Manufacture of metals and metallic alloys by the aluminothermic process.  
184760—Caspar, C. H.—Process of distilling and concentrating liquids.  
191215—Dieterich, H.—Process of manufacturing oxide of barium.  
191233—Soc. of Chemical Industry in Basle.—Manufacture of derivatives of Dihydroisoquinoline.  
191305—Soc. of Chemical Industry in Basle.—Manufacture of azo-dyestuffs.  
191318—Cross, R.—Process for converting hydrocarbon oils into oils of lower boiling point.

*Abstract Published this Week.*

*Titanium dioxide; vanadium compounds.*—Patent No. 189700.—Mr. E. E. Dutt, of 7, Vicarage Gate, Kensington, London, has developed a process for the treatment of the residues of certain bauxites after they have been first treated by the Bayer process for the production of titanium dioxide and vanadium compounds. The residues, after washing, are dissolved in hydrochloric acid to yield a solution containing about 100 grm. titanium chloride per litre. Any considerable excess of acid is then neutralised, the iron is reduced, and alkali acetate added to the solution in amount equal to one-tenth of the titanium chloride present. The solution is boiled to precipitate titanium dioxide, and almost completely neutralised. The filtrate is treated with barium salts to precipitate barium vanadate, which may be used in the preparation of other vanadium compounds.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the official price of 1s. each.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3280.

## SUBSTANCES DISSOLVED IN RAIN AND SNOW.

By H. S. J. FRIES.

Considerable interest has been shown throughout the country on the determination of the character and quantity of substances dissolved in rain and snow. The accompanying article is a continuation of the analyses of rain and snow, which has been carried on at Cornell College for a number of years.

The samples that were analysed were collected in enamelware pans near the centre of the town. The town of Mount Vernon is seventeen miles from Cedar Rapids, the nearest manufacturing centre, and the town itself has no industries of its own.

Forty-one samples of rain and snow were collected and analysed. During the period from September 19, 1921, to June 2, 1922, there was a total precipitation of 17.46 inches of rain, including snows. Twelve inches of snow were taken to equal one inch of rain.

The total pounds of nitrates per acre were 1.074. In order to determine the number of pounds of each substance that fell per acre, we took 226,000 pounds to be the weight of one inch of rain on one acre. We found there were 0.183 pounds of nitrites per acre. The total pounds of free ammonia per acre were 1.843. The total pounds of albuminoid ammonia per acre were 1.327. The precipitation of sulphates as  $\text{SO}_3$  was 0.6919 pounds per acre. The total pounds of chlorine as chlorides was 7.942 per acre.

These analyses were carried on under ordinary laboratory conditions, at the same time avoiding unnecessary contamination during processes. The samples were analysed as soon after their collection as possible.

It is rather interesting to note that the rainfall during the latter part of October, and the latter part of February, was approximately the same, and the highest point reached in each month was exactly the same. Also, the rainfall during December and April was approximately the same, again reaching the same high point in waterfall. This same phenomenon was again observed to be found for the months

of November and March. The high point for these two months was 0.50 and 0.52 inches respectively.

Grateful acknowledgement is made of the kind assistance and suggestions of Dr. Nicholas Knight in carrying on this work.

Cornell College,  
Mount Vernon, Iowa.  
January 20, 1923.

## A METHOD FOR THE NAMING OF ALL ORGANIC COMPOUNDS.

By T. SHERLOCK WHEELER, B.Sc.,  
A.R.C.Sc.I., A.I.C.

The "structure line" system for representing the constitution of organic compounds, described by the author in *The Chemical News*, January 19 and 26, and February 2 (1923, CXXVI, 3275-6-7), is the basis of this new nomenclature system, and in describing the latter, the compounds I., II., III., etc., of the preceding article will be referred to by the same Roman numbers.

Compound I. (*Chemical News*, 1923, CXXV., p. 83) is on the "structure line" system represented by Ar. VI. 2, 3 IV. 2, 3 VI. 4, 5 VI. 2, 3 IV. and its derived name is hexar-2, 3-tetrar-2, 3-hexar -4, 5-hexar 2, 3-tetrar. The number of carbons in a ring shown by the Roman numerals in the representation is, in the name, replaced by the corresponding Greek number followed by "-ar." or "-al." respectively, according as the ring is aromatic or aliphatic. Chains are shown by adding "-an." to the Greek number corresponding to the barred Roman numeral indicating the chain. The termination is adopted because the barred Roman numerals represent fundamentally saturated hydrocarbon chains, and "an" is the usual termination for such chains.

All the rules for the representations apply to the names. Thus everything about a chain or ring comes in brackets immediately after its name; in the chain or ring are included all elements linked to two carbons, and these are shown by their names *before* the number of the place they occupy; the names of groups and elements attached to one carbon come *after* the number of that carbon. Double bonds are called "en" triple "in" as is usual. These syllables precede the number of the ele-

ment from which the double or triple bond starts. It is better not to incorporate these syllables in the chain name, as is done at present, because with several double and triple bonds confusion arises. Branches in the structure line are, in the name, given after the names describing the main line, dashes being used for identification purposes as before. The longest chain or ring system is the one along which, or

through which, the structure line first passes, and the main structure line is made as long as possible. Also Latin numbers are always used to show recurrences of groups, elements, etc., in order to prevent ambiguity with the Greek numbers, cis, trans, and asymmetric compounds are shown as in the representation system.

As the system of representation has been fully described, the method of nomenclature will be clear from the following:—

Number of Compound (in loc. cit.)	Representation.	Name.
II.	Ar. VI. (1-NO <sub>2</sub> , 4-NH <sub>2</sub> ) <sub>2</sub> , 3 V. (4=H <sub>2</sub> ) <sub>2</sub> , 3 V. (2=H <sub>2</sub> ) <sub>3</sub> , 4 IV. (N-2).	Hexar-(1-nitro, 4-amino)-2, 3-pentar-(4-bi-hydro)-2, 3-pentar-(2-bi-hydro)-3, 4-tetrar-(nitrogen-2).
III.	Ar. VI. 3, 4 VI.' 2, 3 VI." 2, 3 VI.; 4', 5' VI.; 4'', 5'' VI.	Hexar-3, 4-hexar'-2 3-hexar''-2, 3-hexar; 4', 5' hexar; 4'' 5'' hexar.
IV.	Al. VI. 3 V.	Hexal-3-pental.
V.	Al. III. 2 $\overline{\text{IV}}$ ' 4 IV.; 2' $\overline{\text{III}}$ . 3 V.; 3' $\overline{\text{III}}$ . (3-Br.)	Trial-2-tetran'-4-tetral; 2'-trian-3-pental; 3'-trian-(3-bromo.)
VI.	$\overline{\text{IX}}$ ' 5 $\overline{\text{IV}}$ .; 4' $\overline{\text{III}}$ . (3-Cl.)	Nonan'-5-tetran; 4'-trian-(3-chloro.)
VII.	$\overline{\text{IX}}$ . (0-3 N-7, 5-Cl, 9=O, 9-OH, $\Delta^7$ .)	Nonan-(oxygen-3, nitrogen-7, 5-chloro, 9-oxy, 9-hydroxy, en-7.)
VIII.	$\overline{\text{V}}$ . (S-3, 3=O.)	Pentar-(sulphur-3, 3-oxy.) (Note): Doubly-linked sulphur corresponding to "oxy" might be called "thio."
IX.	$\overline{\text{IX}}$ . ( $\Delta^5$ ) 5 $\overline{\text{IV}}$ .	Nonan-(bi-en-5 : 8)-5-tetran.
X.	Al. VI. 2, 3 VI. 2, 5 $\overline{\text{III}}$ . (N-2, 2-Me.)	Hexal-2, 3-hexal-2, 5-trian-(nitrogen-2, 2-methyl.)
XI.	Al. VI. 1, 4 XIV.	Hexal-1, 4-tetradecal.
XII.	Ar. VI. 2, 3 VI. 5, 6 VI.	Hexar-2, 3-hexar-5, 6 hexar.
XIII.	Al. VI. 2, 3 VI. 5, 6 VI.	Hexal-2, 3-hexal-5, 6-hexal.
XII. (fully reduced)	Al. VI.' 2, 3 VI. 5, 4' $\overline{\text{V}}$ .	Hexal'-2, 3 hexal-5 4'-pentan.

Number of Compound (in loc. cit.)	Representation.	Name.
XIV.	$\overline{\text{IV.}}$ (1.4 = (OH) <sub>2</sub> , 1:4 $\equiv$ O <sub>2</sub> $\Delta^4$ , 1 trans 4.)	Tetran-(1:4-bi-hydro, 1:4-bi-oxy, en 2 1 trans 4.)
XV.	$\overline{\text{V.}}$ (2-Br. trans 3 NO <sub>2</sub> $\Delta^2$ or + - $\overline{\text{V.}}$ (2-Br., 3-NO <sub>2</sub> $\Delta^2$ ).	Pentan-(2-bromo-trans 3-nitro, en 2) or + - Pentan-(2 bromo, 3 nitro en-2.)
XVI.	$\overline{\text{VI.}}$ (2:3:5 $\equiv$ (OH) <sub>3</sub> , 4- (OH), 1:6=(OH) <sub>2</sub> ) + - or + + - + $\overline{\text{VI.}}$ (1:2:3:4:5:6 $\equiv$ (OH) <sub>6</sub> )	Hexan-(2:3:5-ter hydroxy, 4-hydroxy, 1:6-bi hydroxy.) or + + - + Hexan-(1:2:3:4:5:6- sexi hydroxy.)
XVII.	$\overline{\text{IV.}}$ (2-Cl 3-Br $\Delta^2$ ).	Tetran-(2-chloro, 3- bromo, en-2.)
XVIII.	Probable formula of cinchonine. Al. VI.' (N-4) 4, 1 VI. 3, 3' $\overline{\text{VI.}}$ (0-4) 5 $\overline{\text{II.}}$ 2 Ar. VI. (N-4) 5, 6 VI.	Hexal'-(nitrogen-4)-4, 1-hexal-3, 3'-hexan-(oxygen-4)-5-dian-2-hexar-(nitrogen-4)-5, 6-hexar.

These examples given will suffice to show that the system can supply a systematic name for any compound, no matter how complex, provided its structure be known. It is fundamental in principle since taking no account of the classes of compounds, it names them simply on the basis of structure, chains or rings. It is especially suitable for abstracting, indexing and recording purposes; no longer will it be necessary to give the graphical formula of a compound after its name. It marks another advance in the writing of chemical formulae which passed years ago from the old type system to the graphical linking system, and then stood still. The new method has the

double advantage of enabling a compound to be named from its formula, or alternatively the formula can be deduced from the name.

In *The Chemical News*, 1921, CXXII., 122, the author put forward a logical scheme for the naming of the fundamental groups of organic chemistry. That scheme is very easily fitted into the above; it only necessitates an alteration in the terminations and in the names of some of the groups. In the same paper are indicated methods by which a new system, such as the above, could be introduced into the science of chemistry.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY.]

#### GERMANIUM. IV.—GERMANIUM TETRA-IODIDE.<sup>1</sup>

By L. M. DENNIS AND F. E. HANCE.  
(From the "Journal of the American Chemical Society," December, 1922.)

Winkler<sup>2</sup> prepared germanium tetraiodide by heating pulverulent germanium

in vapour of iodine that was carried over the metal by a slow current of carbon di-

<sup>1</sup> The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

<sup>2</sup> Winkler, *J. prakt. Chem.*, CXLII (N.S. 34), 177, 1886.

oxide. He found it necessary to sublime the product repeatedly in carbon dioxide to remove free iodine. He describes the substance as highly hygroscopic, of orange colour, yellow when powdered, possessing a melting point of  $144^{\circ}$ , and appearing to boil between  $350^{\circ}$  and  $400^{\circ}$ . He gives the results of an analysis of the compound, and adds that L. F. Nilson found that germanium tetra-iodide did not dissociate up to  $440^{\circ}$ , but showed considerable dissociation at  $658^{\circ}$ .

The present investigation describes the preparation and further study of this substance.

*Preparation.*—Powdered, crystalline germanium was placed in alundum boats which were then inserted in a tube of Jena glass lying in an electric combustion furnace. A thermometer was laid in the combustion tube beside the boats. The portion of the tube projecting beyond the furnace was drawn down to small diameter at 7 points 10 cm. apart. Each constriction was packed with glass wool. Into the other end of the combustion tube was inserted the neck of a 500 cc. glass retort containing purified iodine. The tubulus of the retort was joined to an apparatus that supplied pure, dry carbon dioxide. An asbestos box was built around the retort, and this was heated from the outside to a temperature sufficiently high to keep the retort filled with vapour of iodine. The introduction of iodine into the combustion tube was regulated by the rate at which carbon dioxide was passed through the retort.

All air in the apparatus was first displaced by carbon dioxide, and then the retort and tube were gradually heated. Union of germanium and iodine began at  $212^{\circ}$ . When the temperature had risen to  $250^{\circ}$ , there appeared in the hot tube just before it emerged from the furnace a deposit of yellow and red crystals. At  $360^{\circ}$  very rapid combination of germanium and iodine took place, and the sublimate steadily increased until there had collected a considerable deposit of yellow crystals just beyond the boat, and beyond these a mass of orange-coloured crystals on the upper side of the

tube and a ruby-red liquid along the bottom of the tube.

The operation was continued for 30 hours, and at intervals during the run the product that had formed was caused to sublime through the constrictions beyond the furnace by gently heating the tube with a Bunsen flame. It was noted, however, that as the substance was driven through the successive constrictions, its colour gradually changed from bright red (Mulliken's Colour Standard<sup>3</sup> R, Shade 2) to a chocolate-brown (R. O. Shade 2). Inasmuch as this change of colour indicated that the germanium tetra-iodide underwent decomposition when sublimed, the experiment was repeated with a tube that was not constricted, and the red liquid which collected just within and beyond the heated part of the combustion tube was allowed to cool in the tube at the end of the run, which was of 70 hours' duration. It solidified to a mass weighing about 50 g.

During this run there appeared on the walls of the tube, between the last boat and the red tetra-iodide, a deposit of light yellow crystals that were found to be germanous iodide,  $\text{GeI}_2$ . The crystals were of the hexagonal system with external angles of  $120^{\circ}$ . The compound will be fully described in a later article.

*Analysis.*—Portions of the red product were weighed in porcelain crucibles and were moistened with water. Conc. nitric acid was added, and the contents of each crucible was evaporated to dryness on a steam cup. A few drops of conc. sulphuric acid were added, the acid was carefully fumed off, and the crucible was then heated to about  $900^{\circ}$ . The residual germanium dioxide was then weighed.

For the determination of iodine, samples were dissolved in water, 0.1 N solution of silver nitrate was slowly added, and the liquid was vigorously shaken until the yellow precipitate collected and the supernatant liquid became clear. About 3 cc. of conc. nitric acid and a few cc. of a solution of ammonium ferri calum were then added, and the excess of silver was titrated with potassium thiocyanate solution.

Wt. of $\text{GeI}_4$	Wt. of Ge		Wt. of I	
	Calc. G.	Found G.	Calc. G.	Found G.
0.1975	0.02468	0.0243	.....	.....
1.0856	0.13565	0.1357	.....	.....
0.1790	0.02237	0.0225	.....	.....
0.1329	0.0166	0.0165	.....	.....
0.2015	.....	.....	0.1763	0.1761
0.2067	.....	.....	0.1809	0.1807

**Melting Point.**—The measurements were made with a "Tyco's" Precision Thermometer, nitrogen filled, range 100° to 155°. The apparatus was that described by Dennis,<sup>4</sup> which was filled with conc. sulphuric acid. The sample was placed in a small melting-point tube that was attached to the thermometer, and the sulphuric acid was then heated at such rate as to cause a rise of 1° per minute. The yellow, powdered, germanium tetra-iodide assumed an orange tint as the temperature rose, and at 132° it became deep red in colour. It melted sharply to a ruby-coloured liquid at 144°. Repetition of the experiment gave the same result as did a third determination in which was employed an Anschütz thermometer that had been corrected by the Bureau of Standards.

**Crystal Form.**—A crystallographic examination of the substance was kindly made for us by Professor A. C. Gill, of the Department of Mineralogy. The crystals were prepared by slow and careful sublimation in a current of dry, warm air. They were found to be regular octahedrons; the plane angles were 60°, indicating that they belong to the regular system. The crystals showed no double refraction.

**Specific Gravity.**—In searching for a liquid medium in which the specific gravity of germanium tetra-iodide might be determined, its behaviour toward more than 20 inorganic or organic liquids was investigated. In every case the substance was dissolved or decomposed by the liquid. (See Chemical Properties.)

Since the tetrachloride and tetrabromide of germanium had been found to be unaffected by conc. sulphuric acid at room temperature,<sup>5</sup> the behaviour of the tetra-iodide toward this acid was examined, and it was found that at room temperature no visible change could be observed in the substance after submersion in the acid for 24 hours. Consequently, conc. sulphuric acid was used in the determination of the specific gravity of the compound. Pure germanium tetra-iodide was prepared in the form of pellets by spreading the powdered substance along the inside of a long tube of

Jena glass and melting it in a partial vacuum. The temperature was kept below 150°. When the compound melted, it coalesced into small globules about 3 mm. in diameter. A pycnometer of 5 cc. capacity was weighed, was then half filled with the pellets of the tetra-iodide, and was again weighed. Conc. sulphuric acid was now run in until the sample was completely covered, and the air occluded in the pycnometer was then removed by placing the bottle in a vacuum desiccator and exhausting the air. The pycnometer was then filled with sulphuric acid and was again weighed. The specific gravity of the sulphuric acid at the same temperature was determined with the same pycnometer. Two determinations at 26° gave 4.322 and 4.321. Hence  $d_{26}^{26} = 4.3215$ .

**Colour of Germanium Tetra-iodide.**—At room temperature, fused germanium tetra-iodide in lump form is of the colour of coral, the precise shade being "O. R. Normal."<sup>6</sup> When powdered, it has an orange colour "O. Y. Normal."

The compound in lump form shows at various temperatures the colours listed below.

Temp.	Colour.	Mulliken.
-185°	Canary-yellow	O.
- 50°	Buff	Y.O.
- 10°	Orange	O.Y.
+ 35°	Salmon	Y.
+ 50°	Brick-red	O.R.
+ 90°	Red	R.
+144°	Ruby-red	R.O.

**Sublimation of Germanium Tetra-iodide.**—About 5 g. of the substance was placed in a test-tube; in the neck of the tube was inserted a cork that carried a thermometer and inlet and outlet tubes of glass. The test-tube was immersed in an oil-bath, and a slow current of dry air was passed through the tube. The oil was slowly heated. At 110° a yellow vapour appeared in the upper portion of the tube, and as the temperature rose beyond this point a finely crystalline, yellow powder collected on the tube wall. When the tetra-iodide had reached a temperature slightly above its melting point (144°), sublimation was rapid. The heating was then stopped, and the tube was allowed to cool slowly. At the conclusion of the experiment a mass of quite large, orange-coloured crystals had collected on the stem of the thermometer

<sup>3</sup> Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, 1903, Vol. I.

<sup>4</sup> Dennis, *J. Ind. Eng. Chem.*, 1920, XII., 366.

<sup>5</sup> See Dennis and Hance, *Jour. Amer. Chem. Soc.*, 1922, XLIV., 299.

<sup>6</sup> Mulliken's Colour Standards. Ref. 3.

and the unsublimed residue in the tube was of ruby-red colour. It is thus apparent that when germanium tetra-iodide is carefully heated in a current of air to a temperature but slightly above its melting point it sublimes without decomposition.

Nilson and Pettersson have stated<sup>7</sup> that the compound "exists undecomposed in the gaseous condition at 440° but dissociates at higher temperature." They base this statement upon the result of a determination of the vapour density of the compound when it was volatilised at 440° (vapour of sulphur). They obtained a vapour density of 20.46, the theoretical vapour density being 20.0. Our observations during the preparation of germanium tetra-iodide seemed, however, to indicate that the compound is dissociated when heated to temperatures appreciably above its melting point. To gain definite information upon this question glass tubes 1 m. long and 10 mm. wide were sealed at the lower end and were inserted in vertical position into an electric heating furnace to a distance of 20 cm. The tubes were then heated to a temperature of 445°, and a small open tube containing germanium tetra-iodide was dropped into each. In a few minutes a reddish brown vapour appeared in the long tubes just above the top of the electric furnace, and shortly thereafter dark-coloured crystals were deposited on the inner walls of the tube at a distance of about 8 cm. above the top of the furnace. The heating was continued or some time at a temperature between 442° and 448°, and the tubes were then cooled and removed from the furnace. The crystalline deposit 8 cm. above the furnace was identified as free iodine. Just at the top of the furnace there was a deposit of yellow crystals, which proved to be germanium tetra-iodide. Midway between the bottom of the tube and the top of the furnace there was a deposit of canary-yellow crystalline plates of germanium di-iodide.

A small quantity of germanium tetra-iodide was placed in a tube of Jena glass which was then sealed and was gradually heated in an electric combustion furnace to a temperature of 440°. Dissociation resulted, and iodine amounting to over 5 per cent. of the weight of the tetra-iodide was set free.

(To be continued.)

<sup>7</sup> Nilson and Pettersson, *Z. physik. Chem.*, 887, I., 36.

## PROCEEDINGS AND NOTICES OF SOCIETIES.

### THE ROYAL SOCIETY.

THURSDAY, FEBRUARY 15, 1923, AT 4.30 P.M.

Papers read:—

E. R. SPEYER.—*Researches upon the Larch Chermes (Cnaphalopes strobilobius, Kalt.), and their Bearing upon the Evolution of the Chermesinae in general.* Communicated by Prof. G. C. Bourne, F.R.S.

(1) An alternation of form is the normal course of biological development in all *Chermesinae*.

(2) This alternation breaks down at a certain point in the life-cycle of *Cnaphalopes strobilobius*, Kalt., the numerical proportions of one form to another produced in the same generation showing the period at which failure in the alternating mechanism takes place.

(3) The *Progredivens* type of *Cnaphalopes strobilobius*, Kalt., is potentially a winged form, and is not a true dimorphism of the *Sistens* type. This applies also to all *Chermesinae* in which either or both of these types occur.

(4) The *Sexuales* are different morphologically from all other generations. They are held to be a new production in evolution.

(5) Species which are purely parthenogenetic have ceased to develop from an evolutionary point of view, and show the probable course of evolution in the various genera.

(6) Migration from one species of Conifer to another is responsible for a duplication in the series of form-alternating, parthenogenetic generations; the series upon one Conifer has become morphologically different from that on the other through the action of natural selection in two different environments.

(7) In existing species with two host-plants, that portion of the cycle which now takes place upon the definitive host-plant, has arisen through a stimulus given by a recent return to sexuality, this accounting for the linking up of the two cycles and a duplication of the series of parthenogenetic generations.

(8) Under these circumstances the theories of "parallel series" and "polymorphy" become obsolete.

G. V. ANREP.—*The Irradiation of Conditioned Reflexes.* Communicated by Prof. E. H. Starling, F.R.S.

The experiments were performed with tactile conditioned reflexes, the parotid gland being taken as the effector organ. The following facts were established:—

(1) The tactile reflexes established on one side of the animal irradiate without a measurable decrement into the other side of the animal.

(2) There is a progressive decrement in the conditioned reflex during its irradiation over each of the two sides of the animal.

(3) The conditioned inhibition is in broad limits a cruder form of inhibition than the differential inhibition.

(4) The irradiation of the conditioned inhibition follows in the main lines the rules established for the irradiation of the differential inhibition and that of the reflex itself.

(5) The inhibitory processes previously established are temporarily inhibited during the development of a new inhibition.

(6) The short trace reflexes take an intermediate position between the simultaneous and the long trace reflexes.

#### PAPERS READ IN TITLE ONLY.

M. DIXON and H. E. TUNNICLIFFE.—*The Oxidation of Reduced Glutathione and other Sulphydryl Compounds.* Communicated by Prof. F. G. Hopkins, F.R.S.

(1) A study has been made of the sulphydryl compounds: reduced glutathione, cystein and thioglycollic acid. The reduction of methylene blue by these is in each case an autocatalytic reaction.

(2) The active agent producing this catalysis is the disulphide form  $R \cdot S \cdot S \cdot R$ . All the disulphides studied possess the power of catalysing the reduction by each of the sulphydryl compounds.

(3) Evidence is advanced in support of the hypothesis that a more active addition compound of  $R \cdot SH$  with  $R^1 \cdot S \cdot S \cdot R^1$  is formed.

(4) It is shown by three methods that the disulphide compounds also catalyse the oxidation of the sulphydryl compounds by atmospheric oxygen. The form of the reaction curves is not autocatalytic, but an explanation for this is suggested.

(5) The reaction velocity in the cases of glutathione and cystein shows a sharp optimum at a pH of 7.4. Thioglycollic acid does not show this.

(6) The influence of various factors on the reaction is described.

(7) The bearing of these results on the conception of the function of glutathione and related compounds in tissue oxidation processes is discussed.

J. C. BRAMWELL, R. J. S. McDOWALL, and B. A. McSWINEY.—*The Variation of Arterial Elasticity with Blood Pressure in Man.* Communicated by Prof. A. V. Hill, F.R.S.

A method is described by which the extensibility of an artery in living man may be measured at all internal pressures up to the diastolic pressure. As in the case of an isolated artery, the extensibility decreases as the internal pressure is increased.

L. J. HARRIS.—*On the Existence of an Unidentified Sulphur Grouping in the Protein Molecule.* Part I.—*On the Denaturation of Proteins.* Part II.—*On the Estimation of Cystine in certain Proteins.* Communicated by Prof. F. G. Hopkins, F.R.S.

Results obtained by many workers in the past point to the existence of an undiscovered sulphur linkage in certain proteins.

A study has been made of the conditions under which the grouping reactive to nitroprusside is liberated from ovalbumin and other proteins, and of its survival in the proteose, peptone and polypeptide molecule.

The production of this reactive group is an essential feature of the denaturation of ovalbumin and certain other proteins.

The chemical nature of precipitation, denaturation, and coagulation is discussed.

It is suggested that the nitroprusside reaction, attributed by Arnold to cystein, may be due to the presence of a grouping of the thiopeptide type.

A new method has been employed for the gravimetric estimation of cystine in proteins. The results indicate that whereas in serum albumen the cystine accounts for no less than 89 per cent. of the total sulphur content, in ovalbumin 86 per cent. of the sulphur still remains to be accounted for.

Preliminary work has been started on the isolation of sulphur bodies from the degradation products of protein.

N. B. LAUGHTON.—*Reflex Contractions of the Cruralis Muscle in the Decerebrate and Spinal Frog.* Communicated by Sir Charles Sherrington, P.R.S.

(1) In the decerebrate frog there was a prolonged tonic after-effect in the contraction of the cruralis muscle on reflex stimulation of the ipsilateral sciatic nerve. No such tonic effect was observed in the cruralis muscle of the spinal preparation on stimulation of the same nerve.

(2) A shorter latent period and a more rapid increment of height were marked in the spinal preparations.

(3) During spinal shock the height of the reflex contraction in the spinal frog is not maximal.

(4) In 50 per cent. of the experiments the height of the myogram was greater in the decerebrate than in the spinal preparations. In the other 50 per cent. of the experiments, the height of the contractions was greater in the spinal than in the decerebrate frogs.

The Bakerian Lecture was delivered on Thursday, February 22, at 4.30 p.m., by G. I. TAYLOR, F.R.S., and C. F. ELAM, on *The Distortion of an Aluminium Crystal during a Tensile Test*.

#### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

The Annual General Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, February 7, when the President, Mr. P. A. Ellis Richards, delivered his annual address.

The following were elected as Officers and Council for the ensuing year:—

*President*: P. A. Ellis Richards.

*Past-Presidents*, Serving on the Council (Limited by the Society's Articles of Association to 8 in number): Leonard Archbutt, A. Chaston Chapman, Bernard Dyer, Otto Hehner, Samuel Rideal, Alfred Smetham, E. W. Voelcker, J. Augustus Voelcker.

*Vice-Presidents*: F. W. F. Arnaud, F. H. Carr, G. W. Monier-Williams.

*Hon. Treasurer*: Edward Hinks.

*Hon. Secretary*: E. Richards Bolton.

*Assistant Hon. Secretary*: R. G. Pelly.

*Other Members of Council*: H. Ballantyne, S. F. Burford, S. Elliott, B. S. Evans, E. M. Hawkins, Harri Heap, H. F. E. Hulton, Andrew More, A. E. Parkes, W. R. Schoeller, G. R. Thompson, J. F. Tocher.

At the Ordinary Meeting on February 7, 1923, held at the Chemical Society's Rooms, Mr. P. A. Ellis Richards (President) in the chair, certificates were read for the first time in favour of:—Messrs. Joseph John Backes, A.R.C.Sc., A.I.C., D.I.C., Samuel Gordon Stevenson, A.I.C., Richard William Sutton, B.Sc.Tech. (Manch.), A.I.C., Laurence Barnett Timmis, M.Sc.Tech. (Manch.), A.I.C., Alfred Edward Johnson, B.Sc. (Lond.), F.I.C., A.R.C.S.I., Ernest

Victor Jones, F.I.C., Francis Kenelm Donovan, B.Sc. (Lond.).

Certificates were read for the second time in favour of:—Messrs. George Henry Appleyard, F.I.C., James Walter Black, B.Sc. (Lond.), Arthur William Starey, A.R.C.S., B.Sc., A.I.C., John Matthew Wilkie, B.Sc. (Lond.), F.I.C.

The following were elected members of the Society:—Messrs. Henry Aldous Bromley, Walter Horace Clulow, William Penderleith Lewellen Hope, B.Sc. (Edin.), A.I.C., Robert Faraday Innes, F.I.C., Osman Jones, F.I.C., Alan West Stewart, D.Sc. (Brux.), A.I.C., William Heaton Thorns.

The following papers were read:—

*Notes on the Examination of Preserved Meats, etc.*, by OSMAN JONES, F.I.C.

*Titanium in Nile Silt*, by E. GRIFFITHS-JONES.

#### ABSTRACTS.

*Notes on the Examination of Preserved Meats, etc.*, by OSMAN JONES, F.I.C. The author stated that the presence of a trace of zinc chloride in the tin container (which sometimes arises through the use of this salt as a soldering flux) caused a more rapid absorption of tin by the food contents, and that the use of sealing fluid containing a high boiling point solvent caused a disagreeable flavour to be imparted to the food material. Methods for the detection of such a solvent were given. The absorption of tin by the meat contents of a can was found to be the greatest at the time of processing and almost to cease after about four months. The author also mentioned a test for Agar in the presence of gelatine: a dilute solution of iodine in potassium iodide gives a crimson colour with Agar, while with gelatine an orange coloured precipitate is produced.

*Titanium in Nile Silt*, by E. GRIFFITHS-JONES. The author has examined silts from various parts of the Nile, and determined the Titanium by a colorimetric method after freeing the sample from silica. Amounts varying from 1.3 to 2.55 per cent. of titanium oxide on the dried silt were found, but an examination of Egyptian straw, a likely source of titanium, only showed 0.4 per cent. of titanium oxide on the ash.



### THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

Paper read at the Royal Society of Arts on Tuesday, February 13, 1923, at 5.30 p.m.:

*Some Practical Notes on Oil Pumping*, by G. W. E. GIBSON, Member "Koninklijk Instituut van Ingenieurs" (The Hague), Member "Société de Chimie Industrielle" (Paris).

### ROYAL INSTITUTION OF GREAT BRITAIN.

Saturday, February 24.—SIR ERNEST RUTHERFORD, LL.D., D.Sc., F.R.S., M.R.I., Prof. of Natural Philosophy, will deliver his second lecture on *Atomic Projectiles and their Properties*.

### THE CHEMICAL SOCIETY.

On Thursday, February 22, 1923, at 8 p.m., at the Institution of Mechanical Engineers, Storey's Gate, S.W.1, Principal J. C. IRVINE, C.B.E., F.R.S., delivered his lecture, entitled, *Some Constitutional Problems of Carbo-Hydrate Chemistry*.

At the Ordinary Scientific Meeting of the Chemical Society on Thursday, February 15, in addition to the papers announced or reading, Dr. A. SCOTT, F.R.S., made a statement with reference to his investigations on "The Oxide of a New Element" (see *The Chemical News*, this vol., p. 81).

He announced that Coster and Hevesy had found no trace of Hafnium in the samples of sand which he had submitted to them for examination.

Bohr, however, stated that from his spectrum analysis he found lines which did not correspond with any known element.

It is thus possible that two new elements have been discovered.

### THE INSTITUTE OF METALS.

The Annual General Meeting of the Institute of Metals will be held, by kind permission, in the house of the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W.1, on Wednesday and Thursday, March 7th and 8th, 1923. The meeting will commence at 10 a.m. each day, concluding not later than 5 p.m. On March 7th the annual dinner of the Insti-

tute will be held at the Trocadero Restaurant, Piccadilly Circus, W.1, at 7.30 for 8 p.m.

#### May Lecture.

After the Annual General Meeting the next gathering of members will take place, as previously announced, on Wednesday, May 2, at the Institution of Mechanical Engineers, at 8 p.m., when DR. W. ROSENHAIN, F.R.S., will deliver the annual May lecture, his subject being, *The Inner Structure of Alloys*.

#### Annual Autumn Meeting.

The Annual Autumn Meeting of the Institute will be held at Manchester in September. Further announcements regarding both the above meetings will be made at a later date.

### INSTITUTION OF ELECTRICAL ENGINEERS.

An extra meeting was held on Thursday, February 22, 1923, at 6 p.m., when DR. H. W. NICHOLS delivered a lecture on *Transoceanic Wireless Telephony*, followed by a discussion. Mr. B. Welbourn exhibited two cinematograph films on "The Electrification of the Chicago, Milwaukee and St. Paul Railroad Company."

### ROYAL MICROSCOPICAL SOCIETY.

A meeting of the Society was held on Wednesday, February 21, at 7.45 p.m. The following papers were read and discussed:

PROF. SIR WILLIAM MADDOCK BAYLISS, D.Sc., F.R.S., F.R.M.S.: *Microscopical Staining and Colloids*.

MR. A. MALLOCK, F.R.S.: *Note on the Resolving Power and Definition of Optical Instruments*.

### SOCIETY OF GLASS TECHNOLOGY.

A meeting of the Society was held in Armstrong College, Newcastle-upon-Tyne, on Wednesday, February 21, 1923.

The following papers were read:—

*Organising for Production from Pot Furnaces*, by W. W. WARREN, A.M.I.C.E., A.M.I.E.E.

*The Effect of Boric Oxide on the Melting and Working of Glass*, by F. W. HOPKIN, B.Sc., and PROF. W. E. S. TURNER, D.Sc.

*Some Physical Properties of Boric Oxide-Containing Glasses*, by VIOLET DIMBLEBY, B.Sc., S. ENGLISH, M.Sc., and PROF. W. E. S. TURNER, D.Sc.

By the courtesy of the Directors, a visit has been arranged to the works of Messrs. Lemington Glass Works, Ltd., Lemington-on-Tyne, on Wednesday morning, Feb. 21, 1923. The works are engaged in the manufacture of electric lamp bulbs and tubing, the former both by hand and by machine. The furnaces include a recently-installed 10 pot Hermansen Recuperative Furnace. A 24-arm Westlake bulb machine is in operation.

### FUEL PROBLEMS.

On February 6, an open meeting of the Birmingham and Midland Section of the Society of Chemical Industry was held at the University of Birmingham, on "Fuel Problems." Dr. E.B. Maxted, Chairman of the Section, who presided, pointed to the close relationship of fuel and fuel problems to the chemical industry. From a national standpoint our aim should, he said, be to make most effective the utilisation of coal.

Mr. Edgar C. Evans, F.I.C. (London) emphasised the need for fuel problems being considered from a national standpoint. Although our coalfields were geographically crowded together in a very small area, it was a matter for surprise that so few attempts had been made to co-ordinate coalfield problems. Work was being done in the various research laboratories of the country on the constitution of coal, and work had been and was being done at individual collieries, on the particular problems of those collieries, but very little had been achieved towards co-ordinating the mass of individual work available, and drafting in general terms a scheme of research, a method of attack which would be national and not local in its respects. There was necessity for the production throughout the country of a standard blast furnace coke. He believed that the problem of excessive moisture in coke would eventually be solved by the adoption of continuous vertical retorts in which the coke would be evolved inside the oven, so that the only moisture in the material when it reached the furnaces would be that picked up *en route*. The sulphur question was becoming acute in some coalfields. In certain cases, supplies of high-class coking

coal free from sulphur were getting very scarce, and any method of removing it from the remaining seams would be extremely valuable. Sulphur could exist in coal, in one or other of three forms—as pyrites, as organic sulphur and as inorganic sulphur. If it existed as pyrite sulphur it could be reduced very often by crushing the coal to a 10 or 20 mesh size and treating it in a fine coal cleaning plant. In some cases organic sulphur could be very largely reduced by fractional distillations in a current of steam. He had made a large number of tests on different coals in a small retort of about 1 ton a day capacity, in which carbonisation of the coal was effected in a current of superheated inert gas. In some cases where steam was used as the heating medium, considerable reduction of the sulphur content had been effected, but in other instances no improvement whatever took place. There was an enormous opening for smokeless fuel production on a big scale in England, and the gas industry was logically the one that should take up the question. As an example of the possibilities to the gas industry of the preliminary treatment of coal, he cited the following test:—1 ton of coal at 750° C. gave: 70 per cent. of coke containing 5 per cent. of volatiles of a free burning character; 53 to 54 lbs. of sulphate of ammonia; 15 gals. of tar; 4 gals. of light oil; and 17,000 to 18,000 c.f. of gas, of a calorific value of 437 B.T.U.s per cubic foot, the gas not containing more than 10 per cent. of CO. A high yield was not inconsistent with a low carbonising temperature and the production of a high-class smokeless fuel. A national view-point would go a long way, said Mr. Evans, to clear up some great difficulties. The question was primarily one of co-ordination of the research of the country. A chain of research stations was required at the various coalfields; each should specialise in its own problems. Coal owners and iron and steel manufacturers should be on the governing body of the stations, and there should also be gas engineers and fuel consumers. The work should be linked up with that of the universities, and he suggested that the Fuel Research Board should be the central body and co-ordinate researches into a general policy.

Dr. E. W. Smith (F.I.C.), London, said he was of the opinion that gas undertakings should not only supply suitable gas at a low price, but should develop the produc-

tion and sale of smokeless, free burning solid fuel, suitable for domestic and industrial purposes. The net value of the coke available for sale on a gas works was very little different from the net value of the gas made on the works. It was, therefore, well worth while improving the quality of this so-called "by-product," and enhancing its value as much as possible. A number of undertakings certainly did screen and grade their coke, and keep the water content down to a reasonable figure, but more could very well be done. There is room for much to be done in this direction. There was a growing public feeling that "smoke" must eventually be eliminated. All types of coal should be made available for the production of gas and smokeless solid free burning fuel. How could this be attained? By: (1) Coal cleaning; (2) coal blending; (3) coal briquetting; (4) coal briquette carbonisation, and the production of gas and free burning smokeless briquettes. This would be done, and the cycle of operations would be made to pay as compared with present gas works' methods.

Dr. Smith expressed surprise at the action taken by somebody in raising the CO bogie in a newspaper correspondence. The net result of the newspaper stunt had been an increase in the number of people who preferred the "gas way" to end their lives. Ignorance was at the bottom of much of this outcry. It was well that the gas industry was well established, otherwise when it was found that wireless enthusiasts were courting dangers of explosions and fires by earthing their equipments to gas pipes, somebody might demand an inquiry by unbiased men of the highest scientific attainments to advise the Board of Trade whether it was any longer safe for gas to be distributed in houses in iron pipes. It had not been shown that there had been during the last year more accidental deaths from CO poisoning than previously; accidental gas poisoning cases were not more prevalent in districts where the CO was high than where the CO was low, and it had been shown that there was no more CO in towns' gas generally at any time during the last 15 years. Whilst it was important to increase the efficiency of production of fuel, it was more important to increase the efficiency of the utilisation of fuel. That had been done in connection with lighting and gas fires, but much more required to be done in connection with in-

dustrial heating furnaces, and in regard to these he advocated further research work as to insulating materials, conductivity of refractories, the best means of attaining flame temperatures, the value and limits of regeneration, the relative values of radiant heat and thermal efficiencies of standard types of furnaces in use. He believed that the prosecution of such a research would amply repay the Institution of Gas Engineers.

An interesting discussion followed.

#### UNION OF SOUTH AFRICA—DEPARTMENT OF AGRICULTURE.

REPORT OF THE DIVISION OF CHEMISTRY FOR THE YEAR ENDED 30TH JUNE, 1922.

Chief of Division: Chas. F. Juritz, M.A.  
D.Sc., F.I.C.

1. *Organisation.*—The most important function of the year has been that of laying foundations for the closer co-operation of the sections of the Division located in various parts of the Union. This cannot be achieved all at once, but a few select phases of work will be brought into line step by step. Some of these will be enumerated later on. The guiding principle has been the resolution adopted at a conference called by the Secretary for Agriculture of heads of divisions and principals of agricultural schools (shortly before the twelve months under report), viz., that the control and guidance of research work should be vested in the chiefs of divisions, and that the services of the technical officers (i.e., in this case the chemists) at the schools should be utilised to the greatest extent possible to assist the heads of divisions. The relations between the chemists at the schools and the Chief of the Division in regard to research work would therefore rest upon the basic principle that the former should act in a directive capacity, in consultation with the principal of the school concerned, in respect of any work to be carried out by any particular chemist.

At Grootfontein the Division has in Mr. A. Stead an officer of its own: he advises the principal on matters pertaining to the school's chemical section, and in return the school laboratories are at his disposal for the purposes of the Division. On the other hand, the chemist belonging to the school staff assists in the work of the Divi-

sion as far as possible, subsidiarily to the exigencies of the school's own requirements. On this basis the relations between the various chemical laboratories of the Department have been made closer, but a further rapprochement will be needed before a coherent unit is evolved. Meanwhile, consolidation is being proceeded with first where most urgently needed.

The Pretoria laboratory is wholly under the control of the Division. A great deal of the work there carried on hitherto has consisted of soil investigation.

The greatest difficulty is in regard to research work. There the supervision of the Chief of the Division embraces the laboratories attached to the schools as well as those directly connected with the Division. The fullest and most willing co-operation from principals and chemists is given in the endeavours to bring about co-ordination, but development must not be forced. At present measures are taken continuously to inform each institution of the progress of research work at every one of the others. This makes for mutual interest and solidarity of aim. Several problems have arisen and have been dealt with in a satisfactory and uniform manner, that previously would either have been disposed of as the individual institution first confronted therewith thought fit, or left in abeyance until a chemists' conference could consider it.

With the important matter of the agricultural soil survey of the Union little progress has been made. It is impossible for the Chief of the Division to give the survey the undivided attention which is essential, and Mr. Stead, Senior Chemist of the Division, who was placed in charge thereof, was prevented by other duties and prolonged illness from assuming that charge. The work will, it is confidently hoped, soon be commenced.

2. *Commission Work.*—During the year the Chief of the Division served on committees appointed to investigate the problems arising from the need of cheap industrial alcohol, and to inquire into the matter of the destruction of prickly-pear.

From October, 1920, until well into the year under report, Mr. Stead was virtually seconded for service as a member of the Drought Commission. The first-hand knowledge of the country and its problems and conditions gained in the course of this inquiry should prove of great value to the Division.

3. *Publications.*—The following papers by officers of the Division were published during the twelve months:—

A. Stead:

"The Value of the Paddock System," *Journ. Dept. Agric.*, Vol. III., No. 2, August, 1921, pp. 131-135.

B. J. Smit:

"Representative Transvaal Soils: The Norite Black Turf," *Journ. Dept. Agric.*, Vol. II., No. 4, October, 1921, pp. 337-342.

"The Uses of Tobacco Waste," *Journ. Dept. Agric.*, Vol. IV., No. 3, March, 1922, pp. 267-271.

C. F. Juritz:

"The Nicotine-Content of South African Tobacco," *Journ. Dept. Agric.*, Vol. IV., No. 6, June, 1922, pp. 552-562.

"The Submarine Phosphates of the Agulhas Bank," *S.A. Journ. of Industries*, Vol. IV., No. 10, November, 1921, pp. 863-865.

"Bacterial Production of Motor Fuel," *S.A. Journ. of Industries*, Vol. IV., No. 11, December, 1921, pp. 905-910.

B. de C. Marchand:

"On the Volumetric Determination of Phosphoric Oxide," *S.A. Journ. of Science*, Vol. XVII., Nos. 3 and 4, July, 1921, pp. 259-268.

W. J. Copenhagen:

"Studying our Marine Resources," *S.A. Journ. of Industries*, Vol. V., No. 4, April, 1922, pp. 160-163.

EXTRACTS FROM THE REPORTS OF THE  
DIVISION'S OFFICERS IN CHARGE AT  
CAPETOWN, GROOTFONTEIN, AND PRETORIA..

1.—*Capetown: Chief of the Division.*

(a) *Analytical Work.*—During the year 477 samples of various kinds were analysed. Of these, the analyses of salt, brine, bittern, etc., were performed for the purpose of a general survey of the salt-pans of the Union; and an investigation into the nicotine-content of various types and qualities of tobacco grown in the Union was undertaken in connection with the production of a satisfactory tobacco extract. An analysis of ash from tobacco stems yielded 17.8 per cent. of potash.

With the exception of seventeen samples of guano and a few analyses of limestone, practically all the fertilisers analysed were in connection with the Fertilisers, Farm Foods, and Pest Remedies Act.

As usual, several analyses of Government guano were made, and a series of

comparative analyses of the produce of the different islands are also in progress. Limestone from Saldanha Bay crushed for use as agricultural lime was found to contain 36.3 per cent. of carbon dioxide, corresponding to 82.5 per cent. of calcium carbonate. Some limestones and supposed phosphatic deposits from Dassen Island were examined, but the results were not promising.

A special report on the subject of the change in the composition of basic slag was furnished, also one on the alleged poisonous character of basic slag and other fertilisers.

An investigation was commenced, and is being continued, in regard to the relation between the degree of ripeness of grapes and their sugar-content to their suitability for export.

A restricted amount only of soil investigation could be carried out. A sandy soil from the Caledon District was examined and found to be, as such soils usually are, indifferently supplied with humus, low in moisture-retaining power, and poor in plant-food. Two samples of virgin sandy loams from Klipheuvcl were also deficient in organic matter, nitrogen, and water-retaining power as well as in organic plant-food. Some soils from a farm at De Doorns proved to be rather brak, containing about 0.25 per cent. of sodium salts. A similar proportion was found in one out of three soils obtained from a farm in the irrigable area of the Olifants River, Van Rhynsdorp. A very brak soil from Middelburg, Transvaal, was examined. It contained 0.56 per cent. of sodium salts. A deep virgin soil of good humus-content, rich in nitrogen, and with a satisfactory moisture-retaining power, was received from the Ceres District, but its supply of inorganic plant-food could only be described as moderate. Ten soils from the Cradock Division were examined in connection with the construction of an irrigation dam.

The occurrence of collar-rot in citrus trees in the Clanwilliam District led to an examination of the soil for brak salts and acidity. In neither respect was the salt in any way at fault. The use of liquid hydrocyanic acid for the destruction of pests on fruit trees led to an investigation of the character of the liquid commercially applied for the purpose and the mode of its manufacture.

The only sample of water that requires any special remark was one from Bellville,

tested for salinity in connection with its proposed use in dairying. It contained 51.2 parts of dissolved salts per 100,000, consisting almost entirely of sodium chloride.

As to plant products, a sample of *Senecio* from Newlands was examined in connection with its use as a poultry food. Some guinea grass from Somerset East was also analysed with a view to being utilised as fodder. Several plants were examined for their essential oil content, and the constants of those oils determined. Experiments were carried out to ascertain whether prickly-pear sections contain any saponin or pectin substances which could cause it to act as a "spreader" in insecticide washes, but nothing definite could be elicited. It was also sought to ascertain whether prickly-pear mucilage could partially replace gelatine if added when a solution of the latter was just below setting consistency. In this respect, too, the results were of a negative nature.

In connection with experiments at Elsenburg on feeding pigs with the residue of maize from which alcohol had been prepared and distilled off, analyses of mealie meal before and after treatment were carried out.

(b) *Toxicological Work.*—Occasional cases of supposed poisoning of stock were submitted for examination.

Several samples of strychnine were received at various times, with the complaint that they had been found ineffective for wild animal poisoning. In every case the article was found perfectly pure, and the fault must lie in the compounding of the bait.

The deposition of crystals in drums of concentrated sodium arsenite solution was inquired into, and attention given to the numerous untoward results of the careless or malicious use of the arsenicals employed in orchard spraying and stock dipping.

(c) *Microbiological Work.*—In connection with the commercial manufacture of acetone and alcohol from such cultures as maize or sweet potatoes, a bacillus capable of effecting the conversion of maize was obtained by the kindness of the Rockefeller Institute, and cultures were prepared for a large-scale production of these articles, but the plant was not located in a suitable environment, and was subsequently broken up.

Pure cultures of certain soil organisms were procured from the Lister Institute.

and sub-cultures of these were prepared and distributed amongst agriculturists for experimental purposes. Further samples of soil from different parts of the Union were sent to Rothamsted for the study of soil protozoa. Experiments in soil inoculation were initiated on several farms in the south-western districts.

(d) *Dairy Industry Act*.—Under the provisions of this Act, all milk and cream testing appliances offered for sale within the Union have to be tested for accuracy of graduation and dimensions, and marked in a Government laboratory. This practice was continued, and 616 articles examined during the year. They comprised 447 Babcock cream bottles, 72 Babcock milk bottles, and 97 pipettes. Of these, 46.9 per cent. were rejected, viz., 50.1 per cent. of the cream-test bottles, 86.1 per cent. of the milk-test bottles, and 3.1 per cent. of the pipettes.

(e) *Consultation Work*.—On frequent occasions reports had to be furnished on miscellaneous abstract questions submitted for advice, such as the manuring of sandy grass lands, horns as a fertiliser, preservation of foodstuffs, etc.

## 2.—Grootfontein: A. Stead, B.Sc., F.C.S.

Most of the period was occupied by the officer in charge in serving as a member of the Drought Inquiry Commission or on leave of absence. Other work included the inspection of manurial experiments, of brak land at Uitenhage, of prickly-pear spraying tests, of brak in an orchard near Cradock, the compilation of a comprehensive report on brak for the Department of Mines and Industries (still in progress), investigation of the feeding of sheep on prickly-pear as the main portion of their diet, investigation of farmers' experience in the Graaff-Reinet District regarding the utilisation of *Agave americana* as a stock food, experimental feeding of prickly-pear to cows and oxen, and continuation of sheep-feeding experiments.

In connection with the report on brak, referred to above, the methods adopted for reclaiming brak land near Robertson were inspected, and led to a recommendation that the Division of Chemistry should engage in such operations as, for instance, at Klipdrift, where the well-known efforts of the late Mr. J. P. Marais had failed.

A considerable amount of work of an advisory and consulting nature was also done.

## 3.—Pretoria: B. de C. Marchand, B.A., D.Sc.

(a) *Analytical Work*.—The samples received for analysis or examination comprised:—Soils and sub-soils, 146; fertilisers, 115; dairy products, 20; tobacco, 16; water, 15; miscellaneous, 69; total, 381. Of the soil samples, 54 were taken by officers of the Division in connection with investigational work. The only other soil samples which call for any comment were five sent in by the Postal Department in connection with the rapid corrosion of stay rods and plates. This was ascribed to alkaline salts in the soil. Preventive measures were suggested.

(b) *Dairy Glassware*.—The total number of pieces tested was 932, consisting of Babcock cream bottles 583, Babcock milk bottles 277, pipettes 72. The percentage rejected as incorrect was four.

(c) *Investigations*.—In addition to the continuation of others, investigations were commenced on the physical properties of soils, the influence of various factors on the citric solubility of the phosphoric oxide in basic slag, and the determination of "available" potash in soils.

The trials of various methods for the determination of phosphoric oxide in fertilisers were completed, and the results for the sample of basic slag experimented on were published in the *Journal of the South African Chemical Institute*, Vol. V., No. 1, p. 16.

(d) *Pot Experiments*.—In connection with certain of the investigations in hand, pot experiments on a small scale were commenced.

## NOTICES OF BOOKS.

*Outlines of Theoretical Chemistry*, by F. H. GETMAN, Ph.D. Third edition, thoroughly revised and enlarged. Pp. VIII. + 625. New York: Wiley & Sons, Inc. London: Chapman & Hall, Ltd., Henrietta Street, Covent Garden. 1922. Price 18s. 6d. net.

Getman's *Outlines of Theoretical Chemistry* is one of the best of those designed to meet the requirements of students following courses of physical chemistry. It is also a very useful guide and help for those engaged in giving such courses.

A working (but elementary) knowledge of chemistry and physics is naturally assumed. The matter is well arranged, and the re-

sults of recent researches have been incorporated with the subject matter in a very satisfactory manner.

Each chapter is followed by a set of questions which should enable the student to grasp the subject thoroughly.

The author has evidently spared little effort in searching the literature for the important advances that have been made since the earlier editions appeared, and this issue should prove as useful as the previous ones.

(1) *Second Year College Chemistry.*

(2) *Laboratory Manual to accompany Second Year College Chemistry*, by WILLIAM H. CHAPIN. Pp. XI. + 311 and VII. + 112. New York: Wiley & Sons, Inc. London: Chapman & Hall, Ltd., Henrietta Street, Covent Garden, W.C. 1922. Price 15s. net and 7s. 6d.

The trend of chemical science at the present time is reflected by the contents of advanced textbooks, and is, especially in America, directed towards a study of the fundamental principles rather than with the object of adding to the already immense store of facts and methods.

The present volumes by Prof. Chapin indicate this in no uncertain manner, and they are largely devoted to an account of the Chemical Laws and their experimental basis.

The importance of suitable and reliable textbooks of this kind cannot be over-emphasised, since the average student, in his first and early years, is confronted with a mass of descriptive matter and particular facts mixed up hazily in his mind with those theories and generalisations with which they are associated.

Another good feature of the theoretical volume is the adoption of the historical method of treatment. This has led the author to introduce references and brief footnotes dealing with the scientists whose achievements are being discussed in the text. One or two of these require emendation, however.

The same volume contains a prefatory, "Suggested Course of Study," in which the author indicates that the text covers a year's work (32 weeks), and the Laboratory Manual can be used to cover the same period. All the experiments described are stated to have been tested with several classes of students.

In the preface to the Laboratory Companion the author rightly insists on the importance of the careful and correct use

of the laboratory note-books. It often happens that a student is able to derive more knowledge from an unsuccessful experiment than from successful ones carried out casually and written up in an unsatisfactory manner.

Together, these volumes will be found quite suitable for those students for whom they are intended. Those in charge of laboratory classes will find the appendices to the experimental volume of use in planning the work.

*Organic Syntheses*, an annual publication of satisfactory methods for the preparation of organic chemicals. JAMES BRYANT CONANT, Editor-in-Chief. Vol. II., pp. VI. + 100. New York: Wiley & Sons, Inc. London: Chapman & Hall, Ltd., Henrietta Street, W.C. 1922. Price 7s. 6d. net.

The publication of this series, one volume of which is to appear each year, has been undertaken by certain chemists in order to make their detailed directions for the preparation of various organic chemicals available in a permanent form.

The high cost of chemicals, and also the difficulty of obtaining supplies of even ordinary organic reagents during the war caused many researchers to prepare their own.

As frequently happens in such cases, the methods described in compendia and those given in the literature were often found to be unsuitable or at least capable of modification and improvement with regard to yield, cost and facility of preparation.

The results published in this series of "pamphlets" give the experiences and final methods adopted by well-known research workers in certain American Universities, and those of the Eastman Kodak Co. and Parke Davis Co.

The authors do not claim that their methods are ideal, but all have been tested by other experienced organic chemists.

Notes are appended to the methods given, and the original references are quoted.

Undoubtedly the methods of preparation for the 25 bodies described will be found satisfactory, but it is surprising that the authors have retained a slight modification of Skraup's Quinoline synthesis, involving two steam distillations, although in their *Notes* they mention the simpler method of E. de Barry Barnett (*The Chemical News*, 1920, CXXI., 205). Their selection seems to rest upon the fact that the chemists who tested the two processes obtained better re-

sults with the older one—an experience contrary to that of the present writer.

These volumes (Vol. I. appeared early last year, see *The Chemical News*, 1922, CXXIV., 174) should be available in all reference libraries, and they should be consulted by chemists wishing to know of reliable and simple processes for the preparation of moderate quantities of these reagents. J.G.F.D.

#### BOOKS RECEIVED.

*Handbook on Petroleum*, by CAPTAIN J. H. THOMSON and SIR BOVERTON REDWOOD. Pp. XIX. + 342. 1922. Messrs. Charles Griffin & Co., Ltd., Exeter Street, Strand, W.C.2. 12s. 6d. net.

*Organic Syntheses*, by JAMES BRYANT CONANT and Others. Pp. VI. + 100. Vol. II. 1922. Messrs. Chapman & Hall, Ltd., 11, Henrietta Street, Covent Garden, W.C.2. 7s. 6d. net.

*Dyes, and their Application to Textile Fabrics*, by A. J. HALL, B.Sc. (LOND.), F.I.C., F.C.S. Pp. 118. 1923. Sir Isaac Pitman & Sons, Ltd., Parker Street, Kingsway, W.C.2. 3s. net.

*A Method for the Identification of Pure Organic Compounds*, by SAMUEL PARSONS MULLIKEN, Ph.D. Pp. VI. + 238. Vol. IV. 1923. Messrs. Chapman & Hall, Ltd., 11, Henrietta Street, Covent Garden, W.C.2. 30s. net.

#### RAPID ESTIMATION OF IRON AND ALUMINA.

By F. LUCCHESE.

The iron and alumina are precipitated together with ammonia in the presence of ammonium chloride. The precipitate is well washed and dissolved in a known volume of semi-normal sulphuric acid. A few drops of methyl orange solution is now added, and the uncombined acid titrated with semi-normal caustic soda. Then, by difference, one can arrive at the amount of acid used in combining with the iron and alumina. A little concentrated  $H_2SO_4$  is added to the solution, and the iron reduced with  $H_2S$  and subsequently titrated with deci-normal  $KMnO_4$ . From the two titrations the amounts of iron and aluminium oxides can be calculated.—(*Gionale di chim. Ind. App.*, 1923, p. 14).

The February issue of the *Empire Exhibition News*, the organ of the British Empire Exhibition, draws attention to the fact, which statistics have proved, that

after four notable exhibitions boom years have followed, although lean years had preceded these exhibitions



This list is specially compiled for the *Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs, can be obtained gratuitously.

#### Latest Patent Applications.

- 1980—Lland, W.—Production of alkali salts of higher fatty acids. Jan. 22.  
2076—Rusberg, F.—Manufacture of alkali thio-sulphate. Jan. 23.  
2339—Soc. of Chemical Industry in Basle.—Manufacture of dye-stuffs. Jan. 25.

#### Specifications Published this Week.

- 191417—Kulas, C., and Pauling, C.—Process for the manufacture of resinous products of condensation from phenol and formaldehyde.  
171367—Melamid, Dr. M.—Process of producing hydrocarbons of relatively low boiling point from tar oils.  
191582—Haddan, R.—Recovery of aluminium chloride.  
191630—Federal Phosphorus Co.—Production of phosphoric acid.  
176785—Simon, T.—Manufacture of magnesium carbonate from dolomite.  
190995—Legeler, Dr. E.—Process for the manufacture of sulphur proto-chloride.

#### Abstract Published this Week.

*Recovery of hydrocarbons and sulphur from Coal Gas*.—Patent No. 190203.—Badische Anilin & Soda Fabrik; Ludwigshafen-on-Rhine, Germany.  
Coal or coke-oven gas, previously freed from tar, cyanogen compounds, and part of the ammonia content, is passed at ordinary or slightly raised temperature through a number of towers containing active charcoal, such as is obtained by charring wood with zinc chloride. In the first towers, all the benzene hydrocarbons are absorbed; in the next towers, the hydrogen sulphide is removed in the state of free sulphur, after a sufficient amount of oxygen-containing gas with or without ammonia has been added; finally, if desired, the ethylene hydrocarbons are absorbed in the last towers. By employing an arrangement of interchangeable towers, the process may be conducted in a continuous manner. Organic sulphur compounds, if present, are retained in the first towers along with the benzene hydrocarbons; any hydrocyanic acid present becomes converted into ammonium thiocyanate, and is also deposited in the first towers. The ethylene may be freed from ammonia, before or after absorption, by washing with aqueous sulphuric acid or other acid. Instead of absorbing ethylene as such in the last towers, it may be converted into ethylene compounds by interaction with halogens, &c., in the presence of the active charcoal, and these compounds are then retained. The absorbed substances are removed at intervals, for instance, by extraction with a solvent or by expulsion with steam.

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# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3281.

## RUBBER VULCANISATION.

The importance of the new rubber "accelerators" just perfected by British chemists has been explained by Major Lefebure, who is responsible for the development department of the British Dyestuffs Corporation.

He stated, in an interview, that the use of rubber was greatly restricted until about eighty years ago, when Hancock, Goodyear, Parkes and other pioneers discovered that it acquired some very valuable properties when vulcanised, that is, when associated with sulphur. It was only then that rubber began to come into its own; yet, up to some ten years ago, if rubber was needed to combine with sulphur in this way, a temperature of 140 degrees Centigrade or more was required. For a thicker article like ebonite or vulcanite, this temperature had to be maintained for many hours.

About ten years ago, it was discovered that by adding from a quarter per cent. to one per cent. of certain synthetic organic chemicals to the rubber the time of vulcanisation was reduced from one-half to one-eighth, according to the size of the article and the nature of the synthetic organic chemical used. The process was termed acceleration, and it is no exaggeration to say that the use of synthetic organic chemicals in this way has been a landmark in the development of the rubber industry. The consequences are, in the first place, a very appreciable reduction in the amount of steam required in vulcanisation, which means a marked lowering of cost. The use of small percentages of synthetic organic chemicals introduces an entirely new control factor into rubber manufacture.

In America, where the rubber industry is so highly developed, there are very few rubber articles which are not made by the use of these accelerators, but in England we have been slower. An important new feature has now come into the situation. These accelerators are all synthetic organic chemicals which are either actually intermediates in the dyestuffs industry, or can easily be made from such intermediates. We have perfected products with special suitability for different types of rubber. Up to within a year ago it was fairly true to say that the

British rubber industry was largely dependent on chemicals from foreign sources for this purpose. There were certain exceptions. Rubber manufacturers were even using chemicals under trade names without knowing what the chemicals were or without being sure that they could rely on getting them, in say, a year's time if they wanted to repeat them for any particular department of their work. Now that the British chemical industry has taken on the production of them, it will be possible to supply the rubber industry with satisfactory products for all types of rubber production.

Certain important results follow. For example, the range for useful articles in rubber, although wide, has been seriously limited owing to the fact that rubber has had to be vulcanised at 140 degrees Centigrade and over a long period of time. Many materials which would probably compound quite satisfactorily with rubber under less drastic heat treatment have had to be ruled out because of that high temperature. The possibility is now in sight of using such products and a good range of colours, for rubber flooring, hot-water bottles, and so on, is also made possible.

## THE INFLUENCE OF THE ATOMIC NUCLEUS UPON VALENCE, ORIENTATION AND THE INDUCED POLARITY OF ATOMS.

By HERBERT HENSTOCK.

That the hypothesis of the Induced Polarity of Atoms is eminently practical, explaining, as it does, many hitherto obscure and often apparently unrelated phenomena, becomes more and more evident as its applications in various directions are brought to light. Up to the present, with one exception, there does not appear to be any attempt to explain, or attribute any underlying cause to this alternate polarity. The exception referred to is that of Kermack and Robinson (*Trans.*, 1922, CXXI., 427), who assign the cause to the number of electrons in the outer layers of the atoms and not to a precise definition of their supposed arrangement in space. This explanation is, however, only a partial truth and, as will be shown later, does not apply to alternate but to another kind of polarity.

The theory that induced polarity can alter the sign or the electrical effect of an atom, presupposes some easily alterable at-

tribute of that atom, an attribute which does not require any very great force to effect the alteration; for in a chain, say of carbon atoms, once the key atom has its polarity determined, the remainder easily alter their polarities in alternation with the first, each succeeding atom bringing about this effect in its neighbour. This cannot be due to the number of electrons in the octet,

since this is a more or less constant quantity, and is altered only where large forces are brought into play, which may remove an electron from the octet of an atom as in an electro-valence, such forces being much greater than those required for an alteration in alternate polarity. The octets of the atoms in the fluorine<sup>2</sup> molecule may be represented as in Fig. I. The two atoms

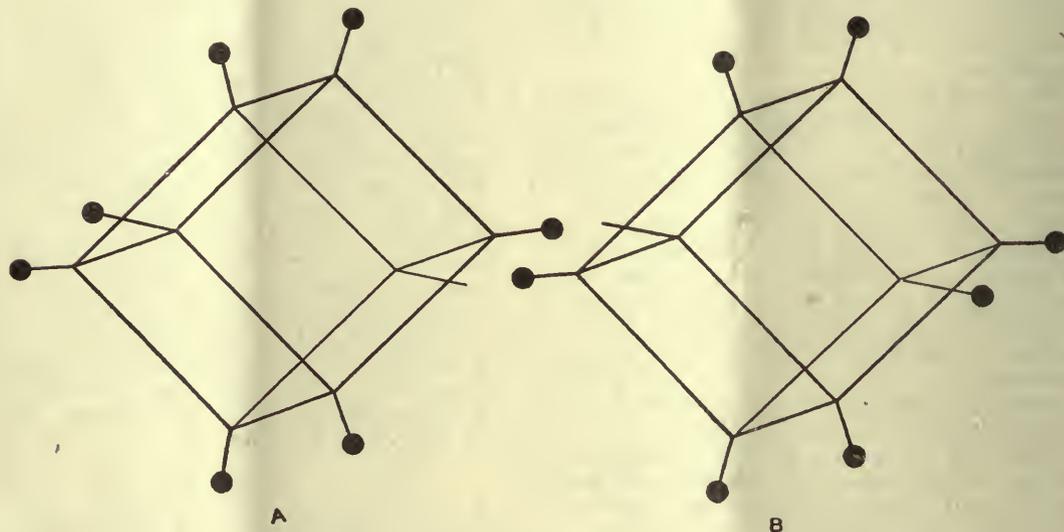


FIG. I.

may share two electrons as a co-valence, but there is no reason why one should be more positive than the other, if the mere numbers of electrons in the outer layers is considered. On the other hand, the author is in agreement with Kermack and Robinson in the view that alternate polarity is not altogether due to the supposed arrangement of the electrons in space. By this process of elimination there remains the nucleus, which, according to Lewis and Langmuir, may be viewed as a di-polar sphere having both poles positive and attended by the inner layer or layers of electrons, most of which are situated at or near the poles. If the nucleus, therefore, with its attendant layers of electrons and their position with respect to the octet be taken

into account, a reason for the opposite polarities may be found. It is possible for the nucleus to rotate within the atom or for the octet to rotate around the nucleus, but when an atom exists in a compound its octet is more or less fixed, so that if there were any rotation it must necessarily be that of the nucleus, which would presumably carry the inner electrons with it. If this rotation<sup>3</sup> be stopped after passing through each angle of  $90^\circ$  there would be two opposing positions for the nuclear poles with respect to the outer layer of electrons: the fluorine atom, discussed above, might be positive or negative according as to whether the nuclear poles and their accompanying electrons pointed in a perpendicular direction, A, or in a horizon-

<sup>2</sup> This element was chosen because its internal construction of nucleus and two electrons is fairly simple, and its octet has only one vacant corner, permitting of but a single normal primary valence bond.

<sup>3</sup> The atom may be normally in a static condition as assumed by Langmuir, but the dynamic condition considered by Bohr may be caused by outside influences, which rotate the nucleus.

tal direction, B (see Fig. II.) with respect to the face a.b.c.d. containing the line a b which forms the edge where a co-valence bond exists. Naming the two nuclear poles, in both A and B, x and y, then if in A the distances between ay and by be called unity, those between ax and bx will be in the ratio

$$\frac{ax}{ay} = \frac{\sqrt{R^2 + \left(\frac{R}{\sqrt{2}} + r\right)^2}}{R^2 + \left(\frac{R}{\sqrt{2}} - r\right)^2}$$

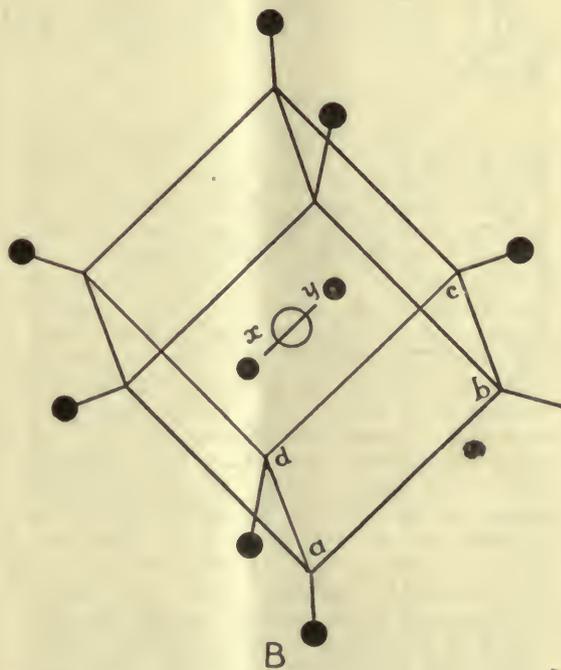
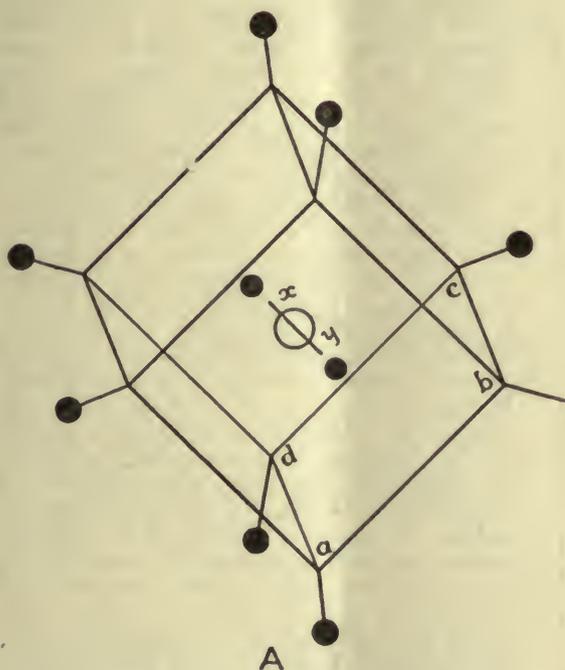


FIG. II.

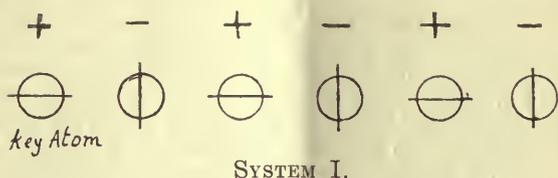
to the former; where  $R$  = radius of sphere occupying the atomic volume and  $r$  = radius of sphere occupying the nuclear volume. On the contrary, in atom B the ratio will be  $ax : by :: 1 : 1$ . Thus the pole y, in A, is at unity distance from b, but the pole x is at a distance greater than unity from (a), whereas in B both these distances are unity. But since the nucleus is by no means saturated or counter-balanced by the inner electrons, the valence bond (a b) in A will have a less quantity of posi-

tive electricity opposed to it than will (ab) in B, and will in consequence attach itself to B, or to any atom constituted like B, the edges (a b) in each making the union. The direction of the nuclear poles in B is such that it will tend to attract electrons to the edge (a b) and to fill up the octet, thus making a stable arrangement which will constitute B a negative atom, and necessarily A will be a positive one.

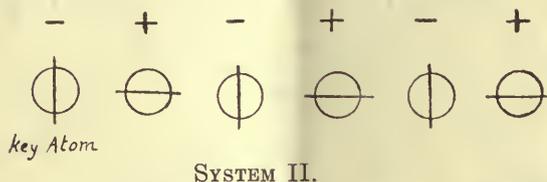
The rigidity of this scheme and of its further applications here set forth, is not insisted upon; it has been used more as a graphic medium for conveying the author's meaning than as an exact picture of what takes place.

It can be stated, therefore, that a strong outside influence may rotate the nucleus of an atom in a chain and so determine its polarity and the atoms directly attached to it will have opposite polarities induced by the rotation of their nuclei, caused by the nucleus of the first atom, which may be looked upon as forces acting at a distance, as assumed by Lapworth (*Mem. Manchester Phil. Soc.*, 1920, LXIV., 1-17; *Trans.*, 1922, CXXI., 416).

Such an alternate polar effect might be shown by considering the nuclei of the atoms without their electrons, somewhat as follows:--



If the polarity of the key atom were altered we should then have the opposite effect, viz.:—



where the poles of the nuclei have been rotated through an angle of  $90^\circ$ .

Particular attention should be given to the fact that there is a fundamental difference between the older conceptions of polarity, as applied to an electro positive or electro negative element in the electro chemical sense, or as applied to ions, and the newer conception of induced polarity. The term polarity, as at present in use, includes two kinds: (1) what might be termed "Permanent-Periodic Polarity" or simply permanent polarity, or that which is due to the greater or less numbers of electrons in the octet, combined with the greater or less strength of the nucleus: this is a permanent periodic function of the elements, running from the single electron and seven vacant spaces in the octets of the strongly electro positive alkali metals to the seven electrons and one vacant space of those of the strongly electro negative halogens, in the usual periods of the periodic table. The formation of ions also may be put down in the same category, for although the ion contains one more or less electron than the atom, nevertheless the formation is confined to the octet, this type of polarity being merely enhanced on passage from atom to ion. The foregoing description is that of the older ideas of polarity. (2) What Lapworth has called "Latent Induced Alternate Polarity," or that which is due to the position of the nucleus with respect to the outer layer of electrons, as has been demonstrated above; this is a variable and transitory condition of an atom depending upon its environment, and it is the immediate cause of the deter-

mination of orientation. The strength of this kind of polarity will, however, be much less than that exerted by the outer electrons, which will determine the electro positive or negative nature of one element to another and not as in this case the polarity of the atoms of the molecule of an element to one another or the alternate polarities of the atoms of a chain. Induced polarity is not a periodic function of the elements; it is overbalanced in the more strongly positive or negative elements in the permanent-periodic sense; such elements as the alkali metals or the halogens scarcely show alternate polarity, which becomes apparent only in the more neutral elements, such as carbon. Lapworth's use of the word "latent," in this connection, is very apposite since either positive or negative alternate polarity may be called into being in an atom, the possibility being inherent in its constitution.

The two types of polarity may perhaps be more clearly seen if considered with respect to a single element. Chlorine is extremely electro negative in permanent periodic polarity, but in its molecule one atom may be weakly positive, the other negative consistently with induced polarity; positive chlorine may therefore exist in a compound. If this assumption of the rotation of the nucleus be extended to the other elements the same simple relationship will be found. Hydrogen has no inner electrons, and is always positive in "permanent periodic polarity": the union of two of its atoms to form a molecule being brought about by the rotation of the nucleus alone, one atom being positive in both kinds of polarity will rotate the nucleus of the second atom, making it negative in alternate polarity, but still remaining positive in permanent polarity. We can therefore have negative hydrogen without any very great bouleversement of our older ideas concerning this element. The inert gases, having no primary valence bonds, cannot exhibit any kind of polarity; they might conceivably display weak alternate polarity, if, as some chemists opine, they can form compounds by means of partial valencies.

Should such compounds be proved to exist, then the inert gases would be capable of exhibiting polar properties which could not be accounted for by means of the older idea of polarity. The remainder of the elements in the series, sodium to fluorine, each having two inner electrons, will act in a fashion similar to that already described

for fluorine, but since they have less numbers of electrons in their octets they will have a larger number of co-valence bonds, each of which will be positive or negative according to the quantity of positive electricity, which the rotation of the nucleus opposes to it in any given condition of the molecule in which atoms of these elements may exist. Carbon, having four electrons symmetrically situated in its octet, will more easily change its induced polarity than will those elements on either side of it; for in any atom the nucleus will tend to set it-

self as symmetrically as possible with respect to the electrons in the octet, and will continually tend to return to such a position when not influenced by outside forces which restrain it; the symmetry of the uncombined carbon octet permits the nucleus to remain in almost any position without strain. Elements of higher atomic weight than those of this series will not change their induced polarity so easily as the latter, since they have a larger number of electrons in their inner layers which will act as a retarding influence.

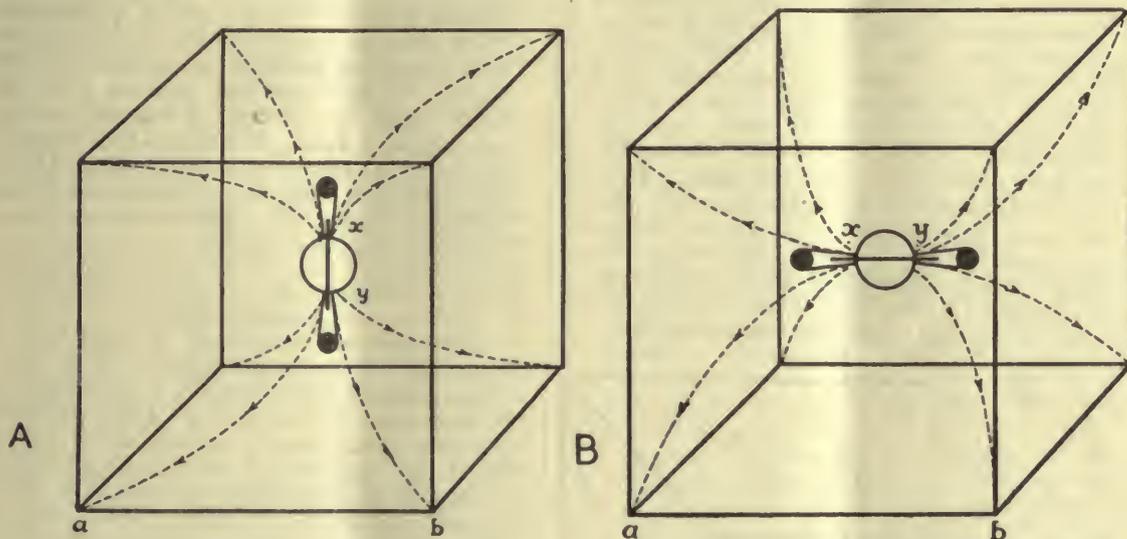


FIG. III.

Before leaving the subject of alternate polarity it may be well to note that the whole idea of the rotation of the nucleus is bound up with that of action at a distance. Actuated by repulsive fields or Faraday tubes of force emanating from the nucleus of a key atom, the nuclei of adjoining atoms are repelled and alter their positions by revolution round their own centres, thus altering the direction of their positive tubes of force (Fig. III.) which is the immediate cause of the alteration in polarity of such atoms. This change in the directions of the tubes of force reacts upon the electrons and vacant corners of the octet with a consequent fluctuation in the powers of attraction at its various parts, which may vary the orientation in the molecule of which the atom is a part, or may even influence the valence of the atom concerned. For tubes of force, see Lapworth (*Trans., loc. cit.*)

#### THE EFFECT OF THE NUCLEUS UPON VALENCE.

If this suggestion be applied to valence, it will be seen that it corroborates, in a remarkable manner, Lewis' and Langmuir's representations.

(1) Electro valence is determined chiefly by permanent polarity. Where a permanently polar, electro negative element, as for example chlorine, which has its octet nearly complete, and tending to final completion by the actual passage of an electron from another atom of a permanently polar electro positive element, say sodium, unites with the latter with formation of an electro valence bond between the two, the negative permanent polarity is so strengthened by the alternate polarity, both acting in the same way, that the united force exerted is sufficient to tear an electron from the octet of the positive sodium, in which both kinds of positive polarity are operating in the same direction (but in an opposite one to that in the negative chlorine), tending to

give up an electron. The action might be compared with the united pull exerted upon the earth by the sun and moon when both are on the same side of the earth. The actual passage of an electron from octet to octet is effected only by the considerable force here exerted, and occurs chiefly between elements strong in permanent polarity, *i.e.*, those near either end of each series or period of the periodic table.

(2) Co-valence is determined by a similar group of forces, but the permanent polarity and alternate polarity combined are not sufficiently powerful to remove an electron from one atom to another, hence a sharing of electrons. The elements, which exhibit co-valence in a supreme degree and rarely display electro valence, are those in which the permanent polarity is weak, and are represented by the ones towards the middle of each period of the periodic table. From the foregoing it is therefore apparent that the only difference between electro valence and co-valence is one of degree, which view is practically identical with that expressed by Briggs (*Trans.*, 1921, CXIX., 1876), and also by Kermack and Robinson (*loc. cit.*)

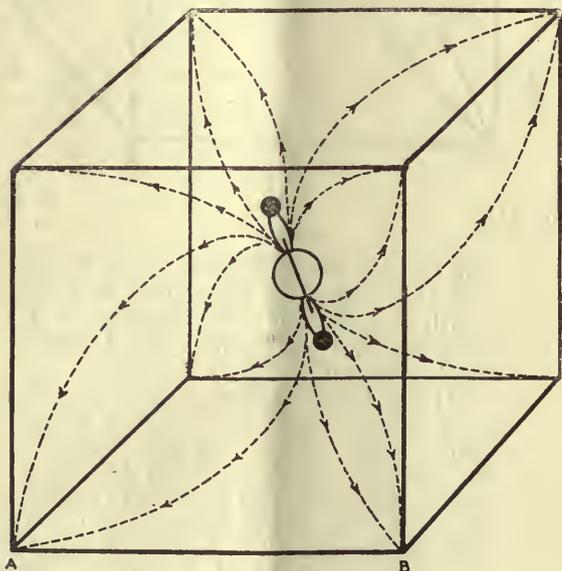


FIG. IV.

The partial valencies discussed by Lapworth and by Kermack and Robinson might be explained on the assumption that the nucleus may be partially rotated through an angle of  $90^\circ$ , *i.e.*, through a fraction of that angle, in some such way as that contemplated in Fig. IV., where the tubes of

force emanating from the nuclear poles will reach the corners of the octet in a different set of directions from, and with forces varying from, those depicted in Fig. III. for primary valence: thus some of the octet corners might be opposed to both nuclear poles, others to but a single one, which would strengthen or weaken their power of attracting electrons, and where such strengthening occurred partial valencies might be possible; each of the corners might or might not be occupied by an electron, and thus a considerable number and variety of possibilities for partial valencies would occur. When a corner of the octet of an atom is unoccupied by an electron and the nucleus is partially rotated so that the tubes of force from both nuclear poles can bear upon this point, a negative partial valence will result, but where the corner is occupied a positive one will occur. This is in agreement with the statement of Briggs (*Trans.*, 1919, CXV., 278) concerning positive and negative affinity.

#### THE EFFECT OF THE NUCLEUS UPON ORIENTATION.

The idea of the rotation or oscillation of the nucleus is not inconsistent with (on a larger scale) the known phenomena of astronomy, and it is more than probable, as has been already assumed by others, that the electrons of the octet, as well as those of the inner layers, oscillate about fixed positions in the atom. Such rotation or oscillation of the nucleus is chiefly dependent upon the strength of forces acting from without the atom, any alteration in these forces would tend to rotate the nucleus wholly so as to alter the polarity of the atom to opposite sign, or partially so as to weaken the existing polar sign. In the case of one atom of a chain of carbon atoms, this would firstly alter the power and direction of the tubes of force operating upon the bonds with side atoms or chains, and might rearrange such bonds, their direction and the consequent orientation on that particular atom also depending to some extent upon the atoms or groups already attached to it; secondly, it would react upon the nuclei of the succeeding atoms with possibly similar results, and so orientation in the molecule would be directly dependent upon the amount of rotation of the various nuclei, the whole resulting from the action of the nucleus of the key atom or atoms, together with the secondary influence of the side chain atoms or groups. For descriptions of the action

of these latter, see papers by Lapworth, Kermack and Robinson, Flurschein, etc. It should be noted, therefore, that the nucleus does not necessarily remain rigidly in the positions indicated in Fig. II., but may oscillate about these positions, so that when a strong key atom influences a chain of atoms, this oscillation may be thereby considerably retarded, or even stopped, when the nuclear poles would face the various edges or corners of the octets, where valence unions are possible, in a more permanent fashion, and so strengthen those positions that such unions would be encouraged. This permanency of position would render the various atomic bonds more positive or negative, and thus more or less reactive, as the case might be, depending upon the polarity of any other reacting atom or group.

The polarity of a group depends to a considerable extent upon the position of the nucleus of that atom, which will affect the union with another group, and since this position is referable to the strength of the key atom or atoms, this is one of the chief agents, which regulates the affinity of groups and in the end their orientation in the molecules they may enter. As an example, the amido and acetyl groups given by Lapworth, will illustrate this. In the amido group the nitrogen is negative in alternate polarity, and similarly in the acetyl group the carbon atom attached to oxygen is positive, consequently the two unite to form acetamide. Again in the  $\text{NO}_2$  group the nitrogen is positive, hence  $\text{NO}_2$  does not unite with  $\text{CH}_3\text{CO}$ . Here, then, we have nitrogen in two groups, negative in one and positive in the other, a phenomenon which is not readily explainable under the older idea of permanent polarity, nor even by a rearrangement of the electrons of the octets of the atoms concerned, but of which a simple solution is afforded by the idea of the rotation of the nucleus underlying alternate polarity as described in the preceding pages. The effect of these two nitrogen-containing groups upon orientation in aniline and nitro-benzene has been shown by Vorländer (*Ber.*, 1919, LII., 263).

The explanations of orientation given by Gough and Thorpe (*Trans.*, 1919, CXV., 1155), and also those by Lapworth and Shoosmith (*Trans.*, 1922, CXXI., 1391) are interesting as demonstrating the ease with which the polarity of the atoms is altered, not merely along a simple chain of carbon atoms, but even through a part of the benzene ring, which goes to show that some easily alterable function of the atoms is

brought into operation, such as might be attributed to nuclear rotation, where little force is needed to affect its alteration.

The author wishes to express his gratitude to Prof. A. Lapworth, for his kindness in criticising this communication, and also for much valuable advice in connection with it.

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[CONTRIBUTION FROM THE DEPARTMENT OF  
CHEMISTRY, CORNELL UNIVERSITY.]

#### GERMANIUM. IV.—GERMANIUM TETRA-IODIDE.<sup>1</sup>

BY L. M. DENNIS AND F. E. HANCE.

(From the "Journal of the American  
Chemical Society," December, 1922.)

(Continued from Page 118.)

From these experiments it would appear that the result of the vapour-density determination at  $440^\circ$  made by Nilson and Petersson showed agreement with the theoretical vapour density not because germanium tetra-iodide does not dissociate at that temperature, but rather because the vapour consists of a mixture of undissociated tetra-iodide and of vapour of iodine which results from the dissociation of the tetra-iodide and which at  $440^\circ$  is diatomic.<sup>2</sup>  $\text{GeI}_4 \rightleftharpoons \text{GeI}_2 + \text{I}_2$ .

Before leaving the point, however, two determinations were made of the vapour density of germanium tetra-iodide with a modified Victor Meyer apparatus.<sup>3</sup> The tube was heated in an electric resistance furnace which made possible the regulation of the temperature within narrow limits,  $442\text{--}446^\circ$ . Taking the temperature as  $445^\circ$ , 0.2827 and 0.6209 g. of substance gave 10.5 and 24.5 cc. of displaced gas at  $0^\circ$  and 760 mm., equivalent to vapour density of 20.87 and 19.67 respectively.

These results show the same agreement with the calculated vapour density, 20.01

<sup>1</sup> The investigation upon which this article is based was supported by a grant from the Heckscher Foundation for the Advancement of Research, established by August Heckscher at Cornell University.

<sup>2</sup> Meyer, *Ber.*, 1880, XIII., 394, 401.

<sup>3</sup> Weiser, *J. Phys. Chem.*, 1916, XX., 532.

as was obtained by Nilson and Pettersson, but crystals of free iodine were found in the inner tube at the close of each determination which proves that germanium tetra-iodide undergoes partial dissociation under these experimental conditions.

*Chemical Properties.*—Winkler<sup>2</sup> stated that germanium tetra-iodide is highly hygroscopic and that it deliquesces when exposed to the air. He found that it first gained in weight (50 per cent. in 1 day), and then lost weight during the next 18 days, the residue then weighing only about  $\frac{1}{4}$  as much as the original sample.

Several different samples of the substance that we have prepared have shown identical properties which are widely different from those that Winkler has described. Germanium tetra-iodide neither gained nor lost appreciably in weight when exposed to the air for 2 days. A sample that weighed 0.5622 g. was allowed to lie on a watch glass exposed to the air of the laboratory for 5 months. At the end of that period its weight had decreased 6.5 mg., and a slight, white incrustation had formed around the sample on the watch glass, but the appearance of the sample was unchanged.

When germanium tetra-iodide is immersed in a small amount of water, it is slowly decomposed with the separation of germanium dioxide, which dissolves when more water is added and forms a clear, colourless solution of acid reaction.

A sample of the compound, placed under conc. sulphuric acid of room temperature, apparently suffered no change in 24 hours, for at the end of that period the acid gave no test for either germanium, or iodine, or for hydriodic acid. When the acid was warmed to 80°, iodine was slowly liberated.

When placed in a 1:4 solution of potassium hydroxide, germanium tetra-iodide is slowly dissolved. Under conc. nitric acid it turns black and nitrogen dioxide is evolved. After standing under the acid for 4 months, the residue still retained its black colour.

Conc. hydrochloric acid of room temperature slowly dissolves germanium tetra-iodide, solution being complete after some weeks. When dropped into conc. ammonium hydroxide, the compound is at once decomposed and decolorised, a white solid being formed. When exposed to dry ammonia gas, the substance is slowly converted into a white powder that is soluble in water.

*Solubility.*—Germanium tetra-iodide dis-

solves without apparent decomposition in the liquids listed below, the solution in each case undergoing no visible change for 4 months.

Solvent.	Colour of solution.
Benzene	Red-orange
Carbon disulphide	Red-orange
Methyl alcohol	Deep orange
Ethylene chloride	Light orange
Monochlorobenzene	Red-orange
Carbon tetrachloride	Light orange
Ethylene glycol	Very light yellow
Ethylene chlorohydrin	Very light yellow

The following solvents dissolved the substance at once, but decomposition slowly took place.

Solvent.	Colour of solution.
Hexane	Orange-red
Amyl alcohol	Deep orange
Chloroform	Pale yellow
Nitrobenzene	Red-orange
Petroleum ether	Pink
Butanol	Orange
Glacial acetic acid	Pale yellow

After standing for 4 months.

Pink (free iodine)
Yellow ppt., brown solution
Reddish yellow solution
White ppt., dark brown solution
Decomposition, black ppt.
Dark brown solution
Dark brown solution

The following liquids decomposed the substance at once.

Acetone	Light brown ppt.
Ether	Ruby-red solution, yellow ppt.
Turpentine	2 liquid layers formed, the upper one a light red, the lower a deep orange; solid residue, dark brown in colour
Oil of lavender	Light yellow ppt. changing to black
Absolute alcohol	Yellow solution, white ppt.
Iso-propyl alcohol	Orange solution, white ppt.
Pyridine	Light yellow solution, white ppt.
Amyl alcohol	Brown solution, white ppt.

#### SUMMARY.

This article deals with the preparation of germanium tetra-iodide, its analysis, the



determination of its melting point, crystal form and specific gravity, its colour at various temperatures, the sublimation and dissociation of the compound, and some of its chemical properties.

*Ithaca, New York.*

### ARABIAN ALCHEMY AND CHEMISTRY.

On Tuesday, February 13, an important lecture on the above-mentioned subject was delivered, under the auspices of the Royal Asiatic Society, by Mr. E. J. Holmyard, the Rt. Hon. Lord Chalmers, G.C.B., presiding.

After expressing his appreciation of the greater interest now shown in the history of science, and emphasising the importance of its study, Mr. Holmyard pointed out that there was a serious gap in our knowledge of the history of alchemy and chemistry. During the period 600-1000 A.D. chemistry was monopolised by Islam. The alchemical MSS. of this period had received but scant attention owing to the difficulties of Arabic. Berthelot had had about thirteen of them translated, but at least three hundred were known and, no doubt, many more existed.

Dealing with the Arabian alchemists individually, on the basis of a first-hand study of the original MSS., Mr. Holmyard dismissed Khalid as incomprehensible. Geber, however, was a man of a very different type, and Mr. Holmyard controverted the views of Berthelot regarding the Latin works ascribed to Geber, and gave reasons for regarding these as genuine translations of works by the Arabian alchemist. Berthelot was acquainted with only a very few of Geber's works, and Mr. Holmyard suggested that these were not, strictly speaking, his chemical works, but mystical writings in which—as a chemist—Geber had employed chemical symbolism to express his religious ideas. The originals of the Latin works ascribed to Geber had not been discovered, but there was an Arabic MS in the British Museum by Geber, entitled the "Book of Properties," which resembled these books in character. The sulphur-mercury theory of the metals was clearly stated in Geber's Arabic works, and the "Book of Properties" contained many practical recipes, such as recipes for the preparation of basic lead carbonate, metallic lead, mercuric sulphide, etc.

The later Arabian alchemists, such as Rhazes, were also briefly dealt with by Mr. Holmyard, who pointed out that, in general, they were men of a practical turn of mind, and illustrations from an Arabic MS in the British Museum, showing the various forms of apparatus used by them, were shown by means of the lantern.

In the discussion which followed, amongst other speakers, Prof. Browne, Dr. and Mrs. Singer, Mr. R. Steele, and Mr. H. S. Redgrove took part. Mr. Redgrove referred to the work that the Alchemical Society, which existed prior to the war, had done to stimulate interest in the history of chemistry. He warmly congratulated Mr. Holmyard on his achievement in substantiating the genuineness of the Latin works of Geber, and raised the question as to the origin of the sulphur-mercury theory, an important factor, in his opinion, being the tendency of the old-time thinkers to base their theories on analogies, not infrequently of an unwarranted character.

### NEW BRITISH CHEMICAL STANDARD.

#### BASIC SLAG "A."

The British Chemical Standards Movement announces the issue of a Basic Slag Standard.

The special uses of this are twofold:—Primarily as an analytical standard for total phosphoric acid and phosphates; and as a standard mainly for basic steel makers, but also for acid steel makers, iron and steel founders and others, to enable them to check their methods for silica, iron, lime and magnesia, etc., in slag.

The analysis is as follows:—Phosphoric Anhydride ( $P_2O_5$ ), 12.93 per cent., equal to Phosphates ( $Ca_3P_2O_8$ ) 28.24 per cent., iron 8.97 per cent., silica 16.15 per cent.

During the standardisation of this slag the need for such a standard has been made abundantly evident to the organisers, for it has been found that even in the determination of such elements as iron, silica, lime and magnesia, which, it may be thought, present little or no difficulty, improvements in methods have been essential in order to get agreement between experienced chemists.

The standard has been tested by a selection of 16 prominent chemists representing

Independent analysts, both metallurgical and agricultural;

The U.S. Bureau of Standards, English and French Iron and Steel Works' Chemists (manufacturers), and English Basic Slag Grinders and Merchants.

It is hoped that chemists will take full advantage of this standard, which has been prepared with the object of promoting unification of analysis.

### GENERAL NOTES.

#### BRITISH INDUSTRIES FAIR.

The vast mass of exhibits to be displayed at the 1923 British Industries Fair at London and Birmingham, between February 19 and March 2, possesses two angles of interest to both home and overseas buyers. The first is covered by the numerous commodities which have only in recent years been produced in Great Britain; the second will be found in the still larger number of exhibits of goods which, while always noted for British quality, will show notable improvements at the Fair, where novelty will be found allied with quality.

In giving the overseas buyer the opportunity to inspect specimens of products and commodities which have only been established in Great Britain during comparatively recent years, the Fair fulfils the first essential of its existence. One of the most interesting sections falling under this class will be that devoted to dyes and fine chemicals. The exhibits in this representative and comprehensive section will range from the rarest of fine chemicals for medicinal and research purposes to those known as "heavies" and sold by the truck load.

#### DYESTUFFS (IMPORT REGULATION) ACT, 1920.

##### BOARD OF TRADE ANNOUNCEMENT.

The total number of applications received during January was 562, of which 473 were from merchants and agents. These were dealt with as follows: Granted, 359; refused, applicants being referred to British makers (British equivalents being available), 94; referred to Reparation supplies, 53; outstanding on January 31, 56.

#### MOROCCO.—PHOSPHATE BEDS.

Mr. C. E. Heathcote-Smith, O.B.E., H.M. Consul at Casablanca, has forwarded to the Department of Overseas Trade the following interesting report on phosphates in Morocco:—

*Extent of Moroccan Phosphates.*—By the discovery of rich and vast phosphate beds, Morocco has become a potential factor of economic importance.

It is credited with the possession of deposits rivalling in extent those of Florida, and in content those of any other country in the Eastern Hemisphere.

Thus the *Oued Zem-El Bouroudj* beds (160 km. south of Casablanca) cover a district of some 75 km. in length and from 5 to 35 km. in breadth. They consist of horizontal layers several metres deep, lying practically on the surface, covering an area of some 400,000 acres, and composed of a fine sand which is nothing other than phosphate of lime of so high a percentage (73 to 78 per cent.) that Florida alone can show similarly rich deposits. Even the bed other than at El Bouroudj also contain a high percentage of phosphates varying from 68 per cent. to 72 per cent. As for their quantity, estimates vary from "many millions of tons" to "hundreds of millions."

It has been calculated that even if the beds were exploited at the rate of several millions of tons annually, centuries will elapse before their exhaustion.

The American rubber-growing proposals are dealt with by a London correspondent of the *Manchester Guardian Commercial* in the last issue. "Quite a number of Americans interested in the rubber trade have been in London lately," he says, "and they are all prophesying a considerable shortage in the visible supplies of rubber before the end of the year. At the same time they are visibly upset at the present price of the commodity, and profess to anticipate higher prices still. It appears to have been suddenly realised that the American is practically dependent upon Britishers for the whole of her rubber needs, and it is being suggested both here and New York that rubber estates on the British plan shall be established in the Philippine Islands by American interests to supply America's needs in the far future. Experts in rubber here ridicule this suggestion. It is pointed out that the Philippines are parcelled out in small tracts for the benefit of the nation,

and that legislation would be needed to alter this system. Again, an American buyer has assured me that the climate is entirely unsuitable, and that the only favourable factor is that Chinese labour for tapping is easily procurable. The same buyer (who is well known in Singapore) admitted that but for British enterprise American rubber users might be paying ten times the price of rubber per pound that they have to do now; he ridiculed the whole idea of Philippine rubber, and hinted that some of his countrymen would do better to pay the market price quietly, as do the cotton buyers in Manchester and Liverpool, instead of getting publicity for themselves over here and incidentally contributing to the tendency for rubber quotations to go still more against their own market."

#### CHEMICAL TRADE WELFARE.

In the House of Commons recently, Mr. Wignall asked the Home Secretary if a welfare order had been issued to the chemical trade, as promised in March, 1922; and, if not, would he say when such an order would be issued to this industry?

Mr. Bridgeman replied that the draft regulations which were referred to in the answer to the question asked by the honourable member on March 27, 1922, were finally made and presented to Parliament in July last, and the great majority of them took effect on October 1. In the case of a few of the regulations, however, strong objection was taken to their immediate enforcement on the ground of the structural alterations involved, and it was agreed, and was provided in the regulations, that the requirements in question should not come into force till April 1 next, or such later date or dates as the Home Secretary might appoint.

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL SOCIETY.

THURSDAY, FEBRUARY 22, 1923, AT 4.30 P.M.

The Bakerian Lecture was delivered by G. I. TAYLOR, F.R.S., and C. F. ELAM, on *The Distortion of an Aluminium Crystal during a Tensile Test.*

The object of the test described was to determine the nature of the distortion

which occurs when a crystal of aluminium is extended by a direct pull, and to find out the relations between the orientation of the crystal axes and the direction of pull.

A rectangular specimen  $1 \times 1 \times 20$  cm. was cut from a round bar of aluminium which had been treated by the method of Carpenter and Elam, so that it consisted of one single crystal. This was stretched through successive extensions of 0, 10, 20, 30, 40, 60 and 78 per cent. of the original length, and at each stage of the test the distortion was determined by measurements of scratches ruled on the surface. At the same time the directions of the crystal axes were determined in each case by X-ray analysis.

The method developed for determining the nature of the distortion, by which any configuration of the specimen was strained into any other, was to find lines of particles which were unextended by the strain. The directions of these lines lie on a quadric cone, which evidently has two positions corresponding with the two configurations from which it was derived.

On applying this method to the specimen under consideration, it was found that for all stages of the extension up to 40 per cent. elongation the "unextended cone" was of a degenerate form consisting of two planes, one of which contained in all cases the same particles, while the other contained different particles for different strains. The former plane was evidently undistorted during the whole strain up to 40 per cent. elongation, and the distortion was due to slipping or shearing over this plane.

The orientation of the crystal axes was determined by X-ray measurements, and it was found that the slip plane was identical with an octahedral (III) plane of the crystal. The direction of the shear was also determined and found to be along one of the three principal lines of atoms in the octahedral plane.

When the specimen was extended beyond 40 per cent. elongation, it was found that the distortion was no longer due to slipping on one plane. This was explained by showing that the effect of the shear was to rotate the axis of the specimen relative to the crystal axes in such a way that another (III) plane came into a position where its inclination to the axis was the same as that of the slip plane. Under these circumstances slipping might occur on both planes simultaneously, and it was verified that this was the case.

THURSDAY, MARCH 1, 1923, AT 4.30 P.M.

Papers read:—

A. MALLOCK, F.R.S. *The Effect of Temperature on some of the Properties of Steel.*

PROF. C. H. LEES, F.R.S. *Inductively Coupled Low Resistance Circuits.*

LORD RAYLEIGH, F.R.S. *Studies of Iridescent Colour, and the Structure producing it. I.—The Colours of Potassium Chlorate Crystals.*

LORD RAYLEIGH, F.R.S. *Studies of Iridescent Colour, and the Structure producing it. II.—Mother of Pearl.*

LORD RAYLEIGH, F.R.S. *Studies of Iridescent Colour, and the Structure producing it. III.—The Colours of Labrador Felspar.*

Paper read in title only:—

L. V. KING, D.Sc. *On the Complex Anisotropic Molecule in Relation to the Dispersion and Scattering of Light.* Communicated by Prof. A. S. Eve, F.R.S.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

The Friday evening discourse on March 2, at 9 o'clock, will be delivered by GEORGE C. SIMPSON, C.B.E., D.Sc., F.R.S., Director, Meteorological Office. The subject is *The Water in the Atmosphere.*

On Saturday, March 3, SIR ERNEST RUTHERFORD, LL.D., D.Sc., F.R.S., M.R.I., Prof. of Natural Philosophy, will deliver his third lecture on *Atomic Projectiles and their Properties.*

#### ROYAL SOCIETY OF ARTS.

On Monday, February 19, DR. H. P. STEVENS, F.I.C., delivered his third Cantor lecture on *The Vulcanisation of Rubber.*

At the Ordinary Meeting on Wednesday, February 21, C. A. MITCHELL, M.A., F.I.C., gave a paper on *Handwriting and its Value as Evidence.*

On Wednesday, February 28, 1923, PROF. W. E. S. TURNER, O.B.E., D.Sc., F.INST.P., Head of the Department of Glass Technology, University of Sheffield, delivered his lecture, entitled *Heat Resisting Glasses.* The Hon. Sir Charles Algonson Parsons, K.C.B., LL.D. D.Sc., F.R.S., presided.

#### THE FARADAY SOCIETY.

At the meeting held on Monday, February 19, the following papers were communicated:—

*Electrolysis with an Aluminium Anode the Anolyte being:* I. *Solutions of Sodium Nitrite;* II. *Solutions of Potassium Oxalate.* By F. H. JEFFERY, M.A.

#### Summary:

With solutions of *sodium nitrite* probably the primary product of reaction at the anode is aluminium nitrite, which is hydrolysed rapidly to hydrated aluminium oxide and nitrous acid, this latter giving rise to nitric oxide and nitric acid.

There is no evidence of the formation of a complex anion of aluminium from these experiments.

With solutions of *potassium oxalate* the product of reaction at the anode is a complex anion derived from aluminium.

The salt  $K_3[Al(C_2O_4)_3] \cdot 3H_2O$  can be derived from the anolytes after electrolysis.

From this mode of derivation it seems very probable that the salt is a true complex salt comparable with potassium chromioxalate.

If this be true, the alumini-oxalate complex can be represented in three dimensions just as Werner represented the chromioxalate. Jaeger resolved the racemic potassium chromioxalate by means of the potassium distrychnine salts. It may be that conditions can be found for the resolution of the alumini-oxalate.

The isolation of a complex salt from an anolyte does not imply necessarily that the constitution of the anionic part of this salt is identical with that of the complex anion present in the anolyte after electrolysis.

An attempt was made to examine the complex anion in solution by the electro-metric method developed for the investigation of the plumbo-nitrite complex  $[Pb(NO_2)_4]$  which was described in a previous paper to the Society. Solutions of potassium oxalate containing a known concentration of the potassium alumini-oxalate were prepared, but an aluminium electrode immersed in such a one had a potential so variable as to be useless for trustworthy determinations; nor were any conditions found to nullify this disability.

*The Law of Distribution of Particles in Colloidal Suspensions, with Special Reference to Perrin's Investigations.* Part II., by ALFRED W. PORTER, D.Sc., F.R.S., F.INST.P., and J. J. HEDGES, B.Sc.

*On a Relation between Surface Tension and Density,* by D. B. MACLEOD, M.A., D.Sc.

*On a Relation between the Viscosity of a D. B. MACLEOD, M.A., D.Sc.*

*On the Viscosity of Liquid Mixtures showing Maxima,* by D. B. MACLEOD, M.A., D.Sc.

#### General Conclusions.

1. The viscosity of liquid mixtures is a

function of the free space of the constituents and of the mixture.

2. In the case of liquid mixtures showing a maximum, the increase of viscosity is due, mainly, to the increase of density, which in turn is due to the chemical affinity between the constituents.

3. It is probable that, complexes which are formed, further reduce the free space and consequently increase the viscosity.

*Electric Potential of Antimony-Lead Alloys*, by S. D. MUZAFFAR.

#### Summary.

Measurements of the electric potential of the antimony-lead-alloys are made by means of a quadrant electrometer against a calomel electrode in normal potassium hydrate solution, normal lead nitrate, and tartar emetic with tartaric acid solutions. The results reveal an identity of potential up to 98 per cent. Sb with that of lead, which show the formation of no solid solution and no chemical compound between the two metals. This work is in agreement with the observations of Charpy, Gautier, Gontermann and Saposchnikoff, and Kanewsky.

### THE CHEMICAL SOCIETY.

ORDINARY SCIENTIFIC MEETING, THURSDAY,  
MARCH 1, 1923, AT 8 P.M.

The following papers were read:—

*Co-ordination compounds and the Bohr Atom*, by N. V. SIDGWICK.

*Silver Salvarsan*, by W. H. GRAY.

*On the Propagation of the Explosion-wave through Gaseous Mixtures*, by H. B. DIXON.

### THE INSTITUTION OF ELECTRICAL ENGINEERS.

#### FARADAY MEDAL.

The Council of the Institution of Electrical Engineers have made the second award of the Faraday Medal to the Honourable Sir Charles Algernon Parsons, K.C.B., F.R.S., Honorary Member of the Institution.

The medal is awarded for "notable scientific or industrial achievement in electrical engineering, or for conspicuous service rendered to the advancement of electrical science."

### THE GEOLOGICAL SOCIETY.

At the Ordinary General Meeting on Wednesday, February 28, 1923, at 5.30 p.m., the following communications were read:—

*The Late Glacial Stage of the Lea Valley (Third Report)*, by SAMUEL HAZZLEDINE WARREN, F.G.S. With a Report on the *Arctic Flora*, by MRS. ELEANOR MARY REID, B.Sc., F.L.S., F.G.S., and MISS MARJORIE ELIZABETH JANE CHANDLER.

*The Elephas-antiquus Bed of Clacton-on-Sea (Essex), and its Flora and Fauna*, by SAMUEL HAZZLEDINE WARREN, F.G.S. With Appendices by Dr. Charles William Andrews, B.A., F.R.S., Mrs. E. M. Reid, and Miss M. E. J. Chandler, Alfred Santer Kennard, F.G.S. and Bernard Barham Woodward, F.L.S., F.G.S., and Martin A. C. Hinton.

### ROYAL MICROSCOPICAL SOCIETY.

The section of the Society formed to deal with the Industrial Applications of the Microscope, and to assist in the development of Industrial Research, met on Wednesday, February 28, 1923, at 7 p.m.

The following demonstrations and exhibits were made:—

Messrs. Charles Baker showed their R.M.S. Microscope (new model).

Mr. Conrad Beck, C.B.E., F.R.M.S., showed Mercury Globules under Polarised Light, with special reference to Dr. Owen's communication read at the last meeting.

Messrs. A. Gallenkamp & Co. demonstrated the use of the Gallenkamp Electrometric Titration Apparatus, an "end point" indicator for all Acid Alkali and Oxidation Titrations.

Messrs. Adam Hilger demonstrated an Interference Accessory for testing the Stands and Fine Adjustments of Microscopes, and also a Vertical Illuminator for the Microscopical Examination of Opaque Objects.

Messrs. Ogilvy & Co. exhibited a Silverman Illuminator for Opaque Objects and Standard Illuminator, both showing similar specimens for comparison of image.

Messrs. W. Watson & Sons, Ltd., showed a Petrological Binocular Microscope for Glass Examination, illustrated by lantern slides.

#### Communications.

Dr. JAMES A. MURRAY, F.R.M.S., in the chair.

MR. HUMPHRY J. DENHAM, M.A., F.R.M.S. (British Cotton Industry Research Association), read a paper, *On Some Mounting Media for Microscopic Objects, especially for Cotton and other Hairs and Fibres, and for general Microscopical Work.*

MR. THOMAS TERRELL, JUNR., read a paper on *The Use of the Microscope in the Gas Mantle Industry*.

#### CORRESPONDENCE.

##### PERUVIAN PETROLEUM.

To the Editor of THE CHEMICAL NEWS.

SIR,—Referring to your issue of January 26, the article upon "Peru: A Land of Mystery" has interested me greatly.

Mention was made of the petroleum deposits around Callas. Although these are really quite productive, and the crude oil of sufficient calorific value to be commercially usable, nothing was mentioned of the vast subterranean fields from one hundred to two hundred and thirty miles north of Iniquitos. It has been the general opinion that these fields do not yield oil of a sufficiently high standard to cover the cost of transport to the coast. The opinion is erroneous. On small holdings, where timber is cut by machinery, most of the well-known makes of internal combustion engines are supplied with the oil in its natural state, the only processes of purification being the passing of the liquid through filters to remove suspended impurities.

The real difficulty lies mainly in the transport of the oil. From the Pestonal Region to the commencement of the coastal region there exists forest-land of almost impenetrable denseness. To convey the oil south to the Amazon would mean long and tedious journeys by river to, let us say, Pernambuco, where it would have to be re-shipped.

In my opinion, however, the fields are sufficiently extensive to warrant the expense of a duct from Pestonal to Lima or Callas, where it could be linked up with the coastal fields. The construction of the necessary plant would pay for itself in time, although the initial cost would be heavy, and the construction period about 18 months.—I am, Sir, Yours, etc.,  
Lowestoft, February 2. C. MELROSE.

##### THE RUHR AND BRITISH DYES.

FROM N. GRATTAN DOYLE, M.P.

To the Editor of THE CHEMICAL NEWS.

SIR,—Whether the commercial community approves or disapproves of the occupation of the Ruhr, that action has had one consequence which must interest not only most men of business as such, but in general the taxpayers of this country. I mean the ban upon German dyes. An embargo has been placed upon the despatch of tar, benzol and the other raw materials

of Germany's dyestuffs industry; lignite, the coal substitute, has been confiscated; transport, whether by rail or Rhine, has been dislocated; and, finally, there comes the announcement that France begins to occupy German dyestuffs factories.

What is happening is not only the isolation of the Ruhr from Germany, but the isolation of Great Britain from German dyestuffs. Is it not fortunate, then, that we have already had the experience of being cut off from German dyes, first during the war, afterwards in the period of disorganisation that followed it? We know where we are; for, if the British textile trades were able, with the help of British dyes, to take the fullest advantage of that post-Armistice boom which was one of the most extraordinary in their history, they will be not less independent to-day, when the range of our dyestuffs is much bigger than it was then. Yet where would we have been now without the Dyestuffs Act, that has made possible an industry on which £200,000,000 worth of our country's trade depends? The enemies of our dyes policy will do well to greet in tactful silence, if not with tardy penitence, this crisis in the Ruhr which, had they been given their way, would certainly have meant a crisis in British factories.—  
Yours, &c., N. GRATTAN DOYLE.  
House of Commons, S.W.1. February 14,

#### NOTICES OF BOOKS.

*Questions and Problems in Chemistry*, by FLOYD L. DARROW. Pp. VII. + 177. London: G. Bell & Sons, Ltd., Portugal Street, W.C. 1923. Price 3s. 6d. net.

In the preface to this collection of over 1,200 questions, the author states that the book is not intended for the use of the teacher, but primarily for the student, as a guide to the every-day preparation of his lessons.

It is certainly true, as is here stated, that many students neglect to prepare their work adequately, but it is very doubtful whether such pupils would remedy this by attempting unaided these questions.

In the main, the questions are instructive, and would stimulate interest. Some of them are beyond the reviewer's ability to answer, and the object of others, also, is not apparent.

*Preliminary Experiments in Qualitative Analysis, with Special Procedures for the Systematic Detection of the Acids*, by LOUIS J. CURTMAN, Associate Professor of Chemistry, Chief of the

Division of Qualitative Analysis, College of the City of New York. Second Edition. Pp. 63. New York: The Elsworth Press. 1922.

The object of this little canvas-covered book is to stimulate the students' interest in qualitative analysis by giving him a preliminary training in the various reactions subsequently utilised in the systematic procedures of qualitative analysis. The student is informed as to the object of the experiments he is to perform, and has to carry out the tests in such a way that the quantitative significance of a reaction is impressed upon him.

The author apparently considers that the systematic procedures for the detection of the metals are beyond the scope of the work, as he does not give them, although he includes, in the appendix, a very satisfactory modification of the analysis of the filtrate after the separation of the metals of the silver group. However, contrary to custom, systematic procedures for the detection of the acid radicals are included. These tables have been compiled largely as the result of investigations carried out in the author's laboratory, and are, certainly, the most outstanding feature of the book.

As a whole, the book can hardly claim to be self-supporting, and the author recommends that it should be used in connection with Baskerville and Curtman's *Qualitative Analysis*, to which numerous references are made. This is a distinct disadvantage, but nevertheless we think that any student would derive great advantage if he worked through this book and did not rest satisfied until he was able to supply a satisfactory answer to all the queries contained within its sixty odd pages. Further, we should like to suggest that many teachers might find this little book very useful as the basis of a catechism for elementary and moderately advanced students of Qualitative Analysis. F.L.S.

The Bureau of Mines and the State of Colorado have jointly issued a Bulletin, entitled *Oil-Shale, a historical, technical and economic Study*, by MARTIN J. GAVIN.

It is pointed out the State of Colorado considers its vast oil-shale deposits of particular value, and in co-operation with the U.S. Bureau of Mines, a research laboratory has been equipped at Boulder, with the object of determining the best conditions of shale distillation.

The bulletin outlines the present status of the petroleum industry, and gives the causes of increased consumption with the possible new sources of supply.

There are sections dealing with the history and nature and origin of oil-shale, the chemistry of its distillation. A good account of the Scotch industry is included, and the whole is well illustrated with numerous figures, graphs, and eighteen plates.

We have received from the British Science Guild a copy of their pamphlet, *Science in National Life*.

It is pointed out that every ounce of scientific knowledge and effort needs to be combined with industrial enterprise if we are to maintain not only our position in the world markets, but also if we are to meet the heavy expenditure incurred by the war.

The breadth, variety and value of the activities carried on in the name of science are seldom realised to the full—if they were, the whole commercial and industrial world would co-operate to encourage the development of scientific investigation and research in all its manifold ramifications. On this foundation we must build, and the foundation must be sound, substantial, and well laid if the superstructure is to compete in strength, beauty, and efficiency with that of other nations.

There is also a plate with the photographs of eight distinguished pioneers of science.

The U.S. Department of the Interior has issued a bulletin (No. 728), entitled *The Occurrence and Uses of Peat in the U.S.*, by E. K. SOPER and C. C. OSBON.

The subject is treated in a very comprehensive manner from both the geological and economic standpoint, and is well illustrated with photographs of typical peat bogs and formations in various States.

It is pointed out that peat is partly decayed and disintegrated plant debris. The salient features of the conversion of cellulose to peat are the elimination of hydrogen and oxygen as water, and of carbon and oxygen as carbon dioxide and the generation of methane.

The authors assign the formula  $C_{62}H_{72}O_{24}$  to peat, and  $C_{72}H_{120}O_{60}$  to cellulose, but give no evidence or authority for this. Peat has been used in agriculture as a nitrogenous fertiliser, and as an absorbent

and disinfectant. It was used, especially during the war, as an antiseptic dressing, and in Bohemia has found application in curative "mud baths." Other uses, apart from the extensive use as inferior fuel, include that as packing material and paper making.

*Chemical Engineering Catalog, 1922:* Seventh Annual Edition. Pp. 1183. New York: The Chemical Catalog Co. Inc., 19, East 24th Street. Price \$10.

To all categories of chemists, not only in America, but in Great Britain as well, this vast catalogue is invaluable. It is very obvious that it has not been compiled solely for individual enterprise, but more as a work of reference. Practically every requirement in chemistry is contained therein, from an 8 cc. platinum crucible to a complete factory; while sections have been added indexing a wide selection of scientific and technical books, and indicating the firms producing fine chemicals.

In the preparation of this enormous work the publishers have been fully alive to its value, and this has greatly guided them. According to the statement made by the compiling Committee, firms are availing themselves of the facilities for using more space, some reserving over 60 pages.

The Committee has been wise in advising advertisers to standardise their respective catalogues, so that anyone using the volume knows precisely where to find what he desires with a minimum of expenditure of time. The copious illustrations and cross-sectional diagrams also fall under this arrangement, tending to eliminate all superfluous data; at the same time, each reproduction is amply ticketed.

The work is certainly very fine; and it is to be hoped that those concerned in the future will do all in their power to maintain the high level reached by the compilers of the seventh edition. J.M.

#### BOOKS RECEIVED.

*Paracelsus: His Personality and Influence as Physician and Chemical Reformer*, by JOHN MAXSON STILLMAN. Pp. X. + 183. 1920. The Open Court Publishing Co., 149, Strand, W.C.2. 10s. net.

A correspondent is desirous of information concerning present prices for:—Hydrochloric acid (pure), sodium oxy chloride, sulphuric acid, and nitric acid, in ton lots.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 2665—Alvord, E. B.—Process of making metal sulphides. Jan. 29.  
 2597—Michell & Co., J.—Manufacture of barium-hydroxide. Jan. 29.  
 2944—Naef, E. E.—Production of compounds of sulphur with alkaline earth metals. Jan. 31.  
 3198—Thermal Industrial & Chemical Research Co.—Removal of matter from surface of a liquid in heat-treatment by molten metal, etc. Feb. 2.

#### Specifications Published this Week.

- 191793—Mai, Dr. A.—Process of making arsenical solutions and suspensions for insecticidal, fungicidal, preservative and like purposes.  
 191854—Imray, O. Y. (Chemical Industry in Basle).—Manufacture of dyestuffs of the triarylmethane series.  
 174599—Soc. L'Azote Francais.—Process for the production of granules of cyanamide with a high nitrogen content.  
 191797—Holliday & Co., Ltd., L. B.—Manufacture of a series of substituted alpha-naphthylamines and of the dyestuffs derived from them.

#### Abstract Published this Week.

- 190688—Chlorides.—Jacobson, B. H., of 1324, Quarriers Street, Charleston, West Virginia, U.S.A.

*Aluminium, antimony, arsenic, iron, tin, zinc, and other chlorides; double chlorides.*—In the production of anhydrous chlorides by the reaction of chlorine on a metal in the presence of bromine, as described in the parent Specification, a salt such as sodium or potassium chloride or bromide is added so as to maintain the product liquid without necessitating a high temperature or pressure. When a bromide is used it is not necessary to add free bromine. The invention is described with reference to aluminium chloride. In an example, aluminium chloride and sodium chloride are melted in a covered iron pot or rotating ball mill and aluminium and bromine are then added, the temperature being suitably 125–150° C. From time to time portions of the melt are drawn off, and more aluminium and salt are added and, when necessary, some additional bromine. The product withdrawn may contain 5 to 30 per cent. of sodium chloride, but is suitable for use in the Friedel-Crafts reaction. If the temperature is maintained at 200° C., aluminium chloride alone is volatilized and is recovered in a condenser.

Messrs. Rayner & Co. will obtain printed copies of the published specifications, and forward on post free for the official price of 1s. each.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3282.

## NOVEL RESEARCH NARRATIVES.

The British Non-Ferrous Metals Research Association has hit upon a rather ingenious way of communicating the results of its research investigations to its members. Lectures are arranged at one or more centres, to which as a rule only the members of the Association itself are admitted. Two objects are served in this manner, firstly early confidential communication of the results of the research is assured to those who have given it financial support, and secondly the investigator gets into close and immediate contact with that section of the industry chiefly interested in his work.

In this manner the future direction of work and the relative practical importance of its varied issues is subjected to the mutual consideration of researcher and the industry.

The Non-Ferrous Metals Research Association is at present engaged on some ten investigations, all of which are closely connected with different branches of the metals and engineering trades.

So far the private lecture system has been applied to two subjects. Dr. W. Rosenhain, F.R.S., has reported on the investigation on Copper and the influence upon its properties of small quantities of impurities, which is being carried out for the Association by Dr. D. Hanson and others at the National Physical Laboratory. This research promises to be of fundamental importance to the copper and brass industry, and most of the leading firms are supporting the work and eagerly take advantage of opportunities, such as this lecture afforded, of hearing the results achieved.

Another large attendance of members was occasioned by the lecture on "The cause and prevention of Red Stains on Brass," by Mr. E. A. Bolton, M.Sc., describing work on this troublesome difficulty which he is carrying out at the Birmingham University—another subject of great practical interest.

The Association arranged a third lecture, given both in Birmingham and Sheffield, by Mr. Dartrey Lewis, M.Met., on his work on "Materials used for the Abrasion and

Polishing of Metals." In view of the wide interests covered, a limited number of tickets was issued to non-members. The Birmingham lecture was held on Monday evening, February 26th, at 7.30 p.m., and the Sheffield lecture on Friday afternoon, February 23rd, at 2.30 p.m.

## NETHERLANDS INTERNATIONAL GAS EXHIBITION.

In connection with the International Gas Exhibition which the Municipal Authorities of Amsterdam are organising, and which is to be held in that city from October 13 to November 11, 1923, H.M. Consul-General at Amsterdam has forwarded to the Department of Overseas Trade copies of the rules and regulations of the exhibition, together with forms of application for space.

It is the intention to collect exhibits demonstrating the use of gas for industrial purposes in large and small concerns, e.g., metal works, chemical works, food preserving factories, restaurants, cycle factories, vulcanising plants, central heating systems, for the practical use of doctors, dentists, bakers, etc. Household and scientific appliances employing gas as fuel will also be welcomed.

British firms interested may inspect the rules, etc., on application to the Department of Overseas Trade (Enquiry Room), 35, Old Queen Street, Westminster, London, S.W.1. A few copies are available for loan to firms unable to arrange for an inspection in London. Ref., 7808/FB/GP.

## REPORT OF THE INTERNATIONAL COMMITTEE ON CHEMICAL ELEMENTS (1923).

### CONSTITUTION OF THE COMMITTEE.

The *International Committee on Atomic Weights* takes its instructions from the International Association of Chemical Societies which was dissolved during the great war and replaced by the *International Union of pure and applied Chemistry*.

During the second Conference, held at Brussels on June 30, 1921, the *International Union of pure and applied Chemistry* decided to replace the *International Committee on Atomic Weights* by an *International Committee on Chemical Ele-*

ments. The scope of the new Committee is more extended than that of the old Committee. The discovery of Isotopy first in the domain of radioactive Elements, later in that of non-radioactive Elements, produced new problems not only concerning Atomic Weights, but also affecting the conception of a chemical Element.

In consequence, the *International Union* has decided that it should be the duty of the new Committee to keep chemists informed of the various advances made each year in this field already rich and so full of promise for the future.

The Committee will therefore prepare three tables: one Table of radioactive Elements containing their principal constants; one Table of Isotopes; one Table of Atomic Weights.

The *International Union* has decided that the Committee should consist of at the most 12 members, and it has itself elected 7 of these: MM. Aston (Great Britain), Brauner (Czecho-Slovakia), Debièrne (France), Ph. A. Guye (Switzerland), Richards (United States of America), Soddy (Great Britain), Urbain (France).

It has appointed as experts for the year 1922 MM. Baxter (United States of America) and Moles (Spain). MM. Clarke and Thorpe are honorary presidents.

The Committee, to complete itself, has, in consequence of the regrettable death of Ph. A. Guye, elected MM. Baxter (United States of America) and Leduc (France). In accordance with its statutes the Committee has invited all the national branches of the *International Union* to create in their countries national Committees from which it may receive notice on any question connected with its activities.

Three of these national Committees are actually working, in Spain, France and Switzerland.

#### WORK OF THE COMMITTEE DURING THE YEAR 1921-1922.

The Committee has prepared the two tables, of which the need was particularly felt: a Table of radioactive Elements, and a Table of Isotopes.

The work of the Committee is not complete as regards the Table of Atomic Weights, which will be published later on. As a result the Table for 1922 drawn up by the old *International Committee for Atomic Weights* is accepted for 1923. It is on this account that the values which appear in the Table of Isotopes under the

title *Atomic Weights* are these given in the International Table for 1922.

In the case of the radioactive Elements the figures appearing under the title *Atomic Mass* are the values, rounded to the nearest whole number, from the Atomic Weights of Uranium (Uranium I), Thorium and Radon (Radium Emanation).

The Committee has found it necessary to modify the nomenclature of several radioactive Elements.

Each of the Tables is accompanied by notes which explain the signs, symbols and new names adopted by the Committee.

The Committee consider that, as regards the radioactive Elements and Isotopes, its work is only provisional. It recognised that the definitions and nomenclatures which have been adopted do not form a homogeneous whole. Until a general reform of the nomenclature of the radioactive Elements is under consideration it has respected as far as possible the names given by the discoverers. On this account, before adopting for the three emanations the names Radon, Actinon and Thoron, the approval of Mme. Curie and Sir E. Rutherford was obtained.

The Committee hopes that the new International Tables will be favourably received by the scientific world, and that the values adopted will be generally approved.

F. W. ASTON.  
GREGORY P. BAXTER.  
BOHUSLAV BRAUNER.  
A. DEBIÈRNE.  
A. LEDUC.  
T. W. RICHARDS.  
FREDERICK SODDY.  
G. URBAIN.

#### INTERNATIONAL TABLE OF ISOTOPES (1923).

*Atomic Number.*—A chemical element is defined by its *atomic number*. This number represents the excess of positive over negative charges in the constitution of the atomic nucleus; theoretically the *atomic number* represents also the number of electrons which rotate round the central positive nucleus of the atom. Each *atomic number* also represents the place occupied by the element in the Mendeléeef Table.

Various methods have been suggested to determine the *atomic numbers*. The most important of these consists in deducing them from the wave-lengths of the high frequency spectra by applying Moseley's law.

*Elements (simple and complex). Isotopes.*—If the above definition is accepted, each chemical element may be *simple* or *complex*, according as its atoms are all of equal mass or not.

In the latter case, the element consists of as many *isotopes* as its *atoms* have different *masses*. A *complex* element is a *mixture of isotopes*. Three methods (J. J. Thomson, Aston, Dempster) have been devised to determine isotopes. The most important is that of Aston.

*Notation.*—The elements, simple or complex, are represented by the ordinary symbols. To indicate any particular isotope its atomic mass<sup>1</sup> is written as an index to the right of the symbol representing the mixture. Thus, Cl<sup>35</sup> indicate the isotope of

chlorine having an atomic mass 35. This number represents the relative mass of its atom, the atom of oxygen (a simple element) being taken as 16.

*Elements included in the Table.*—The isotopes of lead which are the ultimate result of disintegration of radioactive Elements, and the radioactive isotopes will only appear in the International Table of the radioactive Elements. Only those elements appear in the Table of Isotopes which are recognised as simple, or are complex elements whose isotopes have been determined with sufficient certainty.

*Provisional Values.*—Numbers in brackets are to be taken as provisional only.

TABLE OF ISOTOPES.

Element	Atomic number	Atomic Weight	Minimum Number of Isotopes.	Masses of Isotopes	% Accuracy	Observer
H	1	1.008	1	1.008	0.2	A.
He	2	4.00	1	4		A.
Li	3	6.94	2	7 ; 6		A., T., D.
Cl	4	9.1	1	9		T.
B	5	10.9	2	11 ; 10	0.1	A.
C	6	12.005	1	12		A.
N	7	14.008	1	14	0.2	A.
O	8	16.000	1	16		A.
F	9	19.0	1	19	0.1	A.
Ne	10	20.2	2	20 ; 22	0.1	A.
Na	11	23.00	1	23		A.
Mg	12	24.32	3	24 ; 25 ; 26		D.
Al	13	27.0	1	27		A.
Si	14	28.1	2	28 ; 29 ; (30)	0.1	A.
P	15	31.04	1	31	0.2	A.
S	16	32.06	1	32	0.2	A.
Cl	17	35.46	2	35 ; 37	0.1	A.
A	18	39.9	2	40 ; 36	0.1	A.
K	19	39.10	2	39 ; 41		A.
Ca	20	40.07	(2)	40 ; (44)		D.
Fe	26	55.84	(1)	56 ; (54) ?		A.
Ni	28	58.68	2	58 ; 60	0.1	A.
Zn	30	65.37	4	64 ; 66 ; 68 ; 70		D.
As	33	74.96	1	75	0.1	A.
Se	34	79.2	6	80 ; 78 ; 76 ; 82 ; 77 ; 74	0.1	A.
Br	35	79.92	2	79 ; 81	0.1	A.
Kr	36	82.92	6	84 ; 86 ; 82 ; 83 ; 80 ; 78	0.1	A.
Rb	37	85.45	2	85 ; 87		A.
Sn	50	118.7	7 (8)	120 ; 118 ; 116 ; 124 ; 119 ; 117 ; 122 ; (121)		A.
I	53	126.92	1	127	0.2	A.
Xe	54	130.2	7 (9)	129 ; 132 ; 131 ; 134 ; 136 ; 128 ; 130 ; (126) ; (124)	0.1	A.
Cs	55	132.81	1	133		A.
Hg	80	200.6	(6)	(197-200) ; 202 ; 204	0.1	A.

Observers: A = Aston, D = Dempster, T = Thompson (G.P.)

## INTERNATIONAL TABLE OF THE RADIOACTIVE ELEMENTS AND THEIR CONSTANTS.

T	Name	Symbol	Atomic		Isotope	Radiation
			Wt.	No.		
SERIES OF URANIUM AND RADIUM.						
4.67 × 10 <sup>9</sup> years	Uranium I	UI	238	92	U	α
24.6 days	Uranium X <sub>1</sub>	UX <sub>1</sub>	234	90	Th	β
1.15 minutes	Uranium X <sub>2</sub>	UX <sub>2</sub>	234	91	Pa	β (γ)
2 × 10 <sup>6</sup> years	Uranium II	UII	234	92	U	α
6.9 × 10 <sup>4</sup> years	Ionium	Io	230	90	Th	α
1690 years	Radium	Ra	226	88	Ra	α (β+γ)
3.85 days	Radon	Rn	222	86	Rn	α
3.0 minutes	Radium A	RaA	218	84	Po	α
26.8 minutes	Radium B	RaB	214	82	Pb	β (γ)
19.5 minutes	Radium C	RaC	214	83	Bi	99 97% β & γ
10 <sup>-6</sup> second	Radium C'	RaC'	214	84	Po	α
16.5 years	Radium D	RaD	210	82	Pb	(β and γ)
5.0 days	Radium E	RaE	210	83	Bi	β
136 days	Radium F (Polonium)	RaF (Po)	210	84	Po	α (γ)
.....	Radium Ω'	RaΩ'	206	82	Pb	.....
	(Lead)	Pb <sup>206</sup>				
.....	Radium C	RaC	214	83	Bi	0.03% α
1.4 minutes	Radium C''	RaC''	210	81	Tl	β
.....	Radium Ω''	RaΩ''	210	82	Pb	.....
SERIES OF ACTINIUM.						
.....	Uranium ?	....		92	U	α
1.04 days	Uranium Y	UY		90	Th	β
1.2 × 10 <sup>4</sup> years	Protoactinium	Pa		91	Pa	α
20 years	Actinium	Ac		89	Ac	—
19.5 days	Radioactinium	RdAc		90	Th	α (β)
11.4 days	Actinium X	AcX		88	Ra	α
3.9 seconds	Actinon	An		86	Rn	α
2.0 × 10 <sup>-3</sup> second	Actinium A	AcA		84	Po	α
36.1 minutes	Actinium B	AcB		82	Pb	(β and γ)
2.15 minutes	Actinium C	AcC		83	Bi	α
4.71 minutes	Actinium C''	AcC''		81	Tl	β and γ
.....	Actinium Ω''	AcΩ''		82	Pb	.....
SERIES OF THORIUM.						
1.31 × 10 <sup>10</sup> years	Thorium	Th	232	90	Th	α
6.7 years	Mesothorium 1	MsTh1	228	88	Ra	—
6.2 hours	Mesothorium 2	MsTh2	228	89	Ac	β and γ
2.02 years	Radiothorium	RdTh	228	90	Th	α (β)
3.64 days	Thorium X	ThX	224	88	Ra	α
54 seconds	Thoron	Tn	220	86	Rn	α
0.14 second	Thorium A	ThA	216	84	Po	α
10.6 hours	Thorium B	ThB	212	82	Pb	β and γ
60 minutes	Thorium C	ThC	212	83	Bi	65% β
10 <sup>-11</sup> second	Thorium C'	ThC'	212	84	Po	α
.....	Thorium Ω'	ThΩ'	208	82	Pb	.....
	(Lead)	Pb <sup>208</sup>				
.....	Thorium C	ThC	212	83	Bi	35% α
3.1 minutes	Thorium C''	ThC''	208	81	Tl	β and γ
.....	Thorium Ω''	ThΩ''	208	82	Pb	.....
	(Lead)	Pb <sup>208</sup>				
.....	Potassium	K	39.1	19	K	β
.....	Rubidium	Rb	85.5	37	Rb	β

## REMARKS ON THE INTERNATIONAL TABLE OF THE RADIOACTIVE ELEMENTS AND THEIR CONSTANTS.

It is desirable that the nomenclature adopted by the International Commission should be universally accepted, but that now put forward is provisional, serving as a basis for discussion before the ultimate adoption of a standard nomenclature.

T stands for the time in which the quantity of radio-element is diminished to one-half. Under *Radiation*, the brackets ( ) indicate that the radiation is relatively feeble.

<sup>1</sup> The expression "atomic mass" is reserved for isotopes or simple elements considered from the isotopic point of view. The expression ATOMIC WEIGHT retains its

usual meaning, and is applied to elements without consideration of their isotopic constitution.

## CATALYST POISONING.

At the Chemical Society of the University of Birmingham, on February 19—Professor Morgan presiding—Dr. Edward B. Maxted, chairman of the Birmingham and Midland Section of the Society of Chemical Industry, read a paper on "Catalyst Poisoning."

Poisoning may be specific rather than general, the author pointed out, for what is a poison for a given reaction with a given catalyst may be harmless for a second reaction with even the same catalyst or even for the same reaction with a different catalyst.

The following is a summary of Dr. Maxted's remarks:—

1. Catalyst poisoning consists of the preferential adsorption of the poison by the catalyst, in such a way that the secondary valencies of the catalyst, in place of being free for transitory association with the normal reacting system—the probable mechanism of ordinary catalysis—are obstructively saturated by the poison. By obstructively saturated is meant that the free evaporation of the adsorbed poison from the surface of the catalyst and its replacement by the normal reacting system does not take place—or, at all events, not readily.

2. From the above, it follows that if a given inhibitor poisons a given catalyst, then the catalyst will adsorb the poison. The adsorption of a poison by a preliminary charge of catalyst may in some in-

stances be used to purify a reacting system; but in most cases the amount actually removed by a given weight of catalyst is too small for the method to be used practically.

3. The activity of a catalyst during the first stages of poisoning is a linear function of the poison content, and the form of the poisoning curve is intimately connected with that of the adsorption curve.

4. The general type of the reaction curve is not affected by the presence or absence of a poison insufficient in quantity or the complete suppression of activity, provided that the concentration of the poison on the surface of the catalyst does not change during the reaction, and provided also that the form of the catalyst does not change.

## DECOMPOSITION OF FORMIC ACID BY SULPHURIC ACID.

BY E. R. SCHIERZ.

Sulphuric acid decomposes formic acid with the evolution of carbon monoxide, and the velocity of the reaction decreases with addition of water. The reaction is considered to be one of dehydration, an explanation of which is suggested in the equation:—



The effects of other substances on the re-

action have been studied, and whereas both acetone and acetic acid act as diluents, not actually decreasing the dehydrating power of sulphuric acid, if the volume of acetic acid is great, *i.e.*, 1 vol.  $H_2SO_4$  to 10 vols.  $CH_3COOH$ , the formic acid is not decomposed. On the other hand, hydrogen chloride increases the velocity of the reaction. Again, copper, silver, and other sulphates decrease slightly the velocity of reaction.—(*Jour. Amer. Chem. Soc.*, 1923, p. 447.)

### STABILITY OF SODIUM OXALATE SOLUTION.

By E. S. HOPKINS.

In laboratories where oxygen absorption estimations are made, it is frequently the custom to titrate back the excess of permanganate with  $\frac{N}{100}$  sodium oxalate solution. It has been found that this latter is not at all stable, but can be rendered so by the addition of 100 cc.s of 1:4  $H_2SO_4$  to the litre of  $\frac{N}{100}$  oxalate when being made up. Such solution will not deteriorate for two months, even when exposed to daylight in an ordinary colourless glass bottle.—(*Jour. Ind. Eng. Chem.*, 1923, p. 149.)

In his annual report for 1922, George M. Cassatt, President of the American Chamber of Commerce, stated that during 1922 the Chamber continued to use every possible means at its disposal to increase the sale of British products in the United States as well as American goods over here, and in spite of adverse circumstances the results of its efforts demonstrate its importance as a factor in Anglo-American business.

### NOTICES AND PROCEEDINGS OF SOCIETIES.

#### THE ROYAL SOCIETY.

Papers read on Thursday, March 1, 1923, at 4.30 p.m. :—

A. MALLOCK, F.R.S. *The Effect of*

#### *Temperature on some of the Properties of Steel.*

In this paper experiments are described in which the period of torsional vibration and the length of a steel wire were automatically and continuously recorded in terms of time, while the temperature was varied between 15° and 1,000° C., the temperature also being recorded.

From the experiment the variation of rigidity and the coefficient of temperature expansion between these limits can be deduced.

The results show (1) that the variation of the rigidity of steel between ordinary temperature and a dull red heat is small (less than 1 per cent.); (2) that above the critical temperature (about 800° C.) the rigidity decreases rapidly; (3) that the temperature coefficient of expansion does not show any marked change as the metal passes through the critical temperature; but (4) that a comparison with the cooling curves of iron and steel (alluded to in the paper) proves that the specific heat of the high temperature form of the metal is much less than it is at temperatures below the critical point.

PROF. C. H. LEES, F.R.S. *Inductively Coupled Low-Resistance Circuits.*

It is shown that the oscillations in each of two circuits of low resistance coupled by their mutual inductance can be simply expressed in terms of a certain product of capacitance and inductance. The expressions for the currents lead to a simple graphical solution of the problem.

LORD RAYLEIGH, F.R.S. *Studies of Iridescent Colour, and the Structure producing it. I.—The Colours of Potassium Chlorate Crystals.*

The structure of the iridescent potassium chlorate crystals investigated by Stokes and the late Lord Rayleigh is examined microscopically.

The periodic twinned structure inferred by the latter is clearly shown in the photographs taken under the microscope with polarised light.

Some crystals have exceedingly complex structure, showing many groups of evenly spaced twin planes and a very complex reflection spectrum. It is shown that this results from high interference from twinned layers situated a considerable distance apart.

Chlorate crystals, giving a silvery reflection, were obtained by Madan, who heated the ordinary colourless crystals to about

250° C. The complex twinned structure induced by this treatment is investigated, and photographs of the structure of the crystal and of the reflection spectrum are reproduced. There are corresponding irregularities in each, resulting from want of flatness in the twin planes.

LORD RAYLEIGH, F.R.S. *Studies of Iridescent Colour, and the Structure producing it.* II.—*Mother-of-Pearl.*

The structure giving rise to the colour of mother-of-pearl was investigated. The results generally are confirmatory of those given by Brewster and A. H. Pfund. Micro-photographs were reproduced showing the grating structure of a pearl oyster shell and the structure of parallel layers of an "ear" shell. The absorption spectrum of the latter was also reproduced. In agreement with the observed spacing of the layers under the microscope, it shows the reflection to be of the second order.

LORD RAYLEIGH, F.R.S. *Studies of Iridescent Colour, and the Structure producing it.* III.—*The Colours of Labrador Felspar.*

The colours shown by Labradorite felspar were examined experimentally. The colours seen by reflection arise from two distinct origins:—

(1) Specular reflection from tabular inclusions, which show the colours of thin plates and are often as much as 0.2 mm. in dimensions. These are distributed parallel to one of the cleavages.

(2) Diffuse reflection from a plane 15° away from the cleavage mentioned. This is the source of the striking colours which ordinarily excite attention.

When the diffuse reflecting plane is examined microscopically under conditions which ensure that the light only comes from a very thin stratum, it is found that the plane of reflection is discontinuous or patchy. The patches are of irregular outline.

The diffuse character of the reflection is accounted for by the small diameter of these reflecting surfaces, regarded as independent optical apertures. Their size (0.005 mm.) accounts approximately for the angular diameter of the diffuse image of a point source seen by reflection, if we regard this as a diffraction disc. This explanation requires that the reflecting patches, though parallel, should not be strictly co-planar, but distributed at random depth.

The colour of the reflection is not sharply limited to special regions of the spectrum, and it appears that the colour can be explained by the interference of streams of light from the two surfaces of each patch. The patches may be fissures in the material, and there is evidence that their thickness is not absolutely uniform.

The brightness of the colour is explicable by the large number of reflecting patches adding their effects, without definite phase relation such as would give rise to regular interference.

Micro-photographs of the structure giving rise to the two reflections are reproduced.

Paper read in title only:—

L. V. KING, D.Sc. *On the Complex Anisotropic Molecule in Relation to the Dispersion and Scattering of Light.* Communicated by Prof. A. S. Eve, F.R.S.

THURSDAY, MARCH 8, AT 4.30 P.M.

Papers read:—

A. B. WOOD, H. E. BROWNE, and C. COCHRANE. *Determination of Velocity of Explosion Waves in Sea Water. Variation of Velocity with Temperature.* Communicated by F. E. Smith, F.R.S.

P. M. S. BLACKETT. *The Study of Forked Alpha Ray Tracks.* Communicated by Sir Ernest Rutherford, F.R.S.

E. HATSCHKE and P. C. L. THORNE. *Metal Sols in non-dissociating Liquids. I. —Nickel in Toluene and Benzene.* Communicated by Prof. A. W. Porter, F.R.S.

Papers read in title only:—

H. HIRATA. *Constitution of the X-Ray Spectra belonging to the L Series of the Elements.* Communicated by Sir William Bragg, F.R.S.

A. EGERTON. *On the Vapour Pressure of Lead. I.* Communicated by Prof. F. A. Lindemann, F.R.S.

A. C. EGERTON and W. B. LEE. *Some Density Determinations.* Communicated by Prof. F. A. Lindemann, F.R.S.

A. C. EGERTON and W. B. LEE. *Separation of Isotopes of Zinc.* Communicated by Prof. F. A. Lindemann, F.R.S.

#### THE SOCIETY OF GLASS TECHNOLOGY.

Prof. W. E. S. Turner, D.Sc., presided at the meeting held in Armstrong College, Newcastle-on-Tyne, on February 21.

The first paper was: *Organising for Production from Pot Furnaces*, by W. W. WARREN, A.M.I.C.E., A.M.I.E.E. (Manager of Messrs. Lemington Glass Works, Ltd.). The subject was approached from experience gained at Lemington, where methods for producing electric lamp bulbs from pot furnaces were modelled on those in German and Dutch glass works.

Comparing present practice at Lemington with that of 1918, when the output of hand-made pulbs was similar in number and weight, there were now only 20 pots in commission, as against 70 pots in 1918. This intensifying of production had effected an enormous saving of coal. Fuel costs were less than in pre-war times.

During the forenoon, a party of members of the Society visited the glass works at Lemington, and saw in actual operation the scheme outlined by Mr. Warren.

Two other papers were communicated: *The Effect of Boric Oxide on the Melting and Working of Glass*, by F. W. HODKIN, B.Sc., and PROF. W. E. S. TURNER, D.Sc., and *Some Physical Properties of Boric Oxide-containing Glasses*, by VIOLET DIMBLEBY, B.Sc., S.ENGLISH, M.Sc., and PROF. TURNER.

Boric oxide glasses were of great importance. Although boric oxide had been used as a constituent of glass for at least a century, it assumed greater importance from the German researches at Jena forty years ago. Lately, borosilicate glasses had been more in use. The new British chemical glass, American Pyrex glass for chemical and cooking ware, and various illuminating glasses, all contained it. Investigations, designed to lay down a foundation of facts concerning such glasses, were outlined.

Addition of boric oxide to silicate glass increased the durability, but this beneficial effect only held up to a certain point, the maximum benefit for the glass with 20 per cent. of soda being obtained at 11 to 12 per cent. of boric oxide. Glass then became less durable, until when 35 to 40 per cent. was present it dissolved in water. Again, reduction in thermal expansion reached a maximum effect at about 20 per cent. of boric oxide in both series of glasses. The usefulness of boric oxide was limited, and further experiments of the heat-resisting glasses must lie in other directions than the employment of boric oxide. Inversions in annealing temperature, the density, and

refractive index, had also been found at the Department of Glass Technology of Sheffield University.

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#### ROYAL INSTITUTION OF GREAT BRITAIN.

At 3 p.m., on Saturday, March 10, SIR ERNEST RUTHERFORD, LL.D., D.Sc., F.R.S., M.R.I., Prof. of Natural Philosophy, will deliver his fourth lecture on *Atomic Projectiles and their Properties*.

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#### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

The next meeting of the Society will be held on Wednesday, March 7, at the Chemical Society's Rooms, Burlington House, Piccadilly, W., at 8 p.m.

The following papers will be read.

*The Examination of Firearms and Projectiles*, by A. LUCAS, O.B.E., F.I.C.

*The Interpretation of the Results obtained in the Analysis of Potable Waters*, by R. C. FREDERICK.

*Determination of the Purity of Vanillin*, by SYDNEY B. PHILLIPS, A.I.C.

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#### THE INSTITUTION OF ELECTRICAL ENGINEERS.

##### WIRELESS SECTION MEETING.

MR. H. MORRIS-AIREY, C.B.E., gave a lecture entitled *The Development of Naval High Power Valves* on March 7.

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#### THE OPTICAL SOCIETY.

At the meeting held on Thursday, 8th March, the following papers were read:—

*Optical designing as an Art*, by H. DENNIS TAYLOR.

*The distribution of correction duties in Optical Instruments*, by T. SMITH, M.A., F.INST.P.

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#### INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The tenth annual general meeting of the Institution of Petroleum Technologists



will be held at the house of the Royal Society of Arts on Tuesday, March 13th. at 5.30 p.m., and will be followed at about 6 p.m. by a Presidential Address by Professor J. S. S. Brame, F.I.C., F.C.S., the retiring President.

The President-elect for the ensuing session is Mr. Herbert Barringer, M.Inst.-C.E., M.I.Mech.E., M.I.N.A., and the Vice-Presidents are Mr. Alfred C. Adams, Sir George Beilby, Sir John Cargill, Viscount Cowdray of Cowdray, Mr. Arthur W. Eastlake, and Sir Thomas H. Holland.

### INSTITUTE OF CHEMISTRY.

At the 45th Annual General Meeting of the Institute of Chemistry, held at 30, Russell Square on March 1, the President, Mr. A. Chaston Chapman, F.R.S., in presenting the Report of the Council, remarked on the progress of the organisation of the profession of chemistry under the Institute. The roll of Fellows and Associates had increased during the past twelve months by 421, to a total of 4,062, and the register of students by 72, to a total of 955.

The Institute was taking an increasing part in the affairs of the country, and was frequently appealed to by Government Departments and other authorities for advice and help. Natural Science—and in this connection chemistry must be given a position of prominence—was by far the most important dynamic factor in human progress. Notwithstanding its liability to abuse, its discoveries had made enormously for the greater good and happiness of the human race. Science was coming into its own, and scientific men would be given their proper status and rightful place in the affairs of the country. The Institute, in common with other societies and associations, was actively promoting a spirit of solidarity among all concerned with chemistry.

The direct utilisation by the State of the services of the professional chemist was a matter not only of immediate concern to chemists themselves, but was of high importance to the community, and in the country's interests no less than in those of its members, the Institute was bound to do all it could to ensure that the relations between the appointing authorities and those who held official chemical positions were satisfactory. Unfortunately, some public

bodies did not appear to be aware of the lengthy and expensive nature of the chemist's training, or of the difficulties and responsibilities connected with his work, and consequently the Institute sometimes found the advertised conditions of certain public bodies were not commensurate with the importance of the services demanded. The mere saving of money was not always identical with true economy, and it was clearly of public importance that men of good general education, of high professional attainments, and of high moral character should be chosen to fill these positions, while it was obvious that appointing authorities would seriously limit the field for selection, unless the conditions offered were such that men of the right class would be willing to accept. For the appointment of public analyst the remuneration offered was often entirely inadequate and, in some cases, even below that paid before the war.

The Institute had also been obliged to complain of the competition of state-aided institutions with private practitioners, and it was a source of gratification that the Ministry of Agriculture and Fisheries had recognised the legitimate grievance of the private practitioner, and had taken steps towards limiting the agricultural work done in the institutions receiving its grants to that required for strictly educational purposes or necessary to the advisory work of the institutions.

The disinterested zeal of the scientific worker was something without parallel in the whole world, but it was not wise for any country to presume too much on this disinterestedness. Science was one of the greatest and freest of all givers, but it had a right to demand that it should receive that recognition and that proper position in the councils of the country to which it was entitled.

A leading German industrial chemist had said lately that, notwithstanding Germany's position of virtual bankruptcy, the State had come to the help of the great chemical and physical societies, like the Kaiser Wilhelm Institute, and if the State could not continue financial aid the German people themselves must give their last mark to maintain science.

Referring to the prospects of the profession, the President said chemistry had great attractions for most boys, and there were many induced by a liking begotten in

the school laboratory to embark upon a profession for which they had perhaps no real aptitude. A chemical career was not a succession of fascinating experiments, but it involved a good deal of hard work of a comparatively unattractive character, made very great demands on its devotees, and called for much self-sacrifice on the part of those who adopted it as a profession. The profession had attracted a larger number of young men during the last four years than in any previous corresponding period, but he was optimistic in regard to the future. It was a remarkable fact that, notwithstanding industrial depression, the new members of the profession were being steadily absorbed. This absorption might be taken as an indication that chemistry was more highly valued by manufacturers than formerly. Leaders of industry were turning more to science to assist them in solving their problems.

The Report of the Council and Financial Statements were received and adopted, and the officers, Council, and censors for the ensuing year were elected.

The Meldola Medal was awarded, for the second time, to Dr. Christopher Kell Ingold.

## SOCIETY OF CHEMICAL INDUSTRY.

### BIRMINGHAM AND MIDLAND SECTION.

At the meeting on February 20, the following papers were delivered:—

*Interaction of Formaldehyde and the Nitronaphthylamines*, by PROFESSOR GILBERT T. MORGAN (Head of the Chemical Department of the University), and F. R. JONES.

The authors state that the seven known nitronaphthylamines have been condensed with formaldehyde under varying conditions:— 4-nitro- $\alpha$ -naphthylamine and 2-nitro- $\alpha$ -naphthylamine give dinaphthylmethane bases; 1-nitro- $\beta$ -naphthylamine furnishes the hydrolysable methylenebis-1-nitro- $\beta$ -naphthylamine, which exists in two differently coloured modifications; 5-nitro- $\beta$ -naphthylamine gives rise to two products, a dinaphthylmethane base and a dinaphthacridine; 8-nitro- $\beta$ -naphthylamine gives methylenebis-8-nitro- $\beta$ -naphthylamine, which becomes transformed into a dinaphthylmethane base; 5-nitro- $\alpha$ -naphthylamine resembles  $\alpha$ -naphthylamine in yield-

ing ill-defined products, whereas 8-nitro- $\alpha$ -naphthylamine furnishes methylenebis-8-nitro- $\alpha$ -naphthylamine and a dinaphthylmethane base which has the noteworthy property of separating in yellowish white tabular crystals containing three molecular proportions of formaldehyde.

These results show that the nearer the nitro-group is to the amino-radicle in the nitronaphthylamine the more marked is the retarding effect of this nitro-group on the condensation with formaldehyde.

*Note on the Preparation of  $\beta$ -Naphthol-4-sulphonic Acid*, by PROFESSOR MORGAN and EVELINE JONES.

An attempt has been made to obtain  $\beta$ -naphthol-4-sulphonic acid from the commercially available naphthalene-1-diazo-2-oxide-4-sulphonic acid by boiling this diazo-compound with alcohol, when elimination of the diazo-group occurs, the resulting  $\beta$ -naphthol-sulphonic acid being characterised by means of its azo-derivatives with the diazonium salts of *p*-toluidine, *p*-nitroaniline and  $\beta$ -naphthylamine.

S. R. CARTER, M.Sc., Chemistry Department of the University, read a paper on the *Concentration of Hydrogen Ion*. The advantages of reducing all degrees of acidity and alkalinity to one common scale were demonstrated, and the basis of Sørensen's Hydrogen Ion experiment ( $P_h$ ) was explained. The constitution of indicators was discussed and their application to the determination of  $P_h$  values was illustrated by experiments. The latter portion of the lecture was devoted to the electro metric methods employed for hydrogen ion measurements, and to electro metric titrations and the principles involved were illustrated by reference to potentiometers and electrodes lent by the Cambridge and Paul Instrument Co.

## GENERAL NOTES.

### VERTICAL RETORTS AND CHEMICAL PROBLEMS.

Mr. Joseph Poulson, F.C.S. (Stafford Corporation Gas Works) read a paper on "Experiences of Vertical Retorts," before the members of the Midland (Junior) Gas Engineers, at the Birmingham Council House, on Thursday, January 14. He gave

the following particulars of the tar produced:—

Per ton of coal carbonised ... 17.3 gallons.  
Specific gravity of tar ..... 1.095  
Water content of tar ..... 3.5 per cent.  
Free carbon in tar ..... 3.1 per cent.

*Sulphate of Ammonia.* — Twenty-three lbs. of neutral dry quality, testing 25½ per cent. of ammonia are obtained per ton of coal carbonised. Ammonia is at present allowed to go forward to the purifiers to assist in purification.

Since the commencement of operation of the vertical retorts, the district has been remarkably free from naphthalene, and there has not been recorded one single complaint from this cause for over 3¼ years. The naphthalene content of the gas is 0.85 grain per 100 cubic feet. The freedom from such deposit has permitted the installation of a station meter of the Rotary type, but further information regarding this is not yet available, the meter having been in operation only a few months.

No pitching troubles have been experienced. The collecting mains are run off daily, and before opening the valve to effect this, any accumulation of thickened matter that has drained to the exit end of the main is scooped out. The amount of thick tarry matter obtained from each main daily averages 14 to 16 lbs. The period of draining of each main is about three-quarters of a minute. After closing the draining valve, the collecting main is then filled to the level of the weir overflow with warm and weak liquor supplied from an overhead tank. The temperature of the gas from the retorts is 185° C., and of the gas, near the outlet of the collecting main, 118° C.

As to the refractory materials used in the settings, he stated that examination of the materials proved them to be remarkably true to size and shape. The surfaces were smooth, and edges well defined. The fracture of portions of the various segments revealed a uniformity of texture. Small nodules of unconverted quartz were evenly disseminated throughout the mass. The materials used in the construction of the floors of the combustion chambers were of close texture, and the strength of the materials was good, when taking into consideration their composition. The following are analyses of the various portions used:—

## SILICA RETORT SEGMENTS.

	per cent.
Silica .....	89.27
Titanic Oxide .....	0.77
Alumina .....	8.53
Ferrie Oxide .....	0.84
Manganese Oxide .....	—
Magnesia .....	0.23
Lime .....	—
Potash .....	0.20
Soda .....	0.30
Loss .....	0.05

## COMBUSTION CHAMBERS.

	per cent.
Silica .....	91.60
Titanic Oxide .....	0.46
Alumina .....	6.32
Ferrie Oxide .....	0.30
Manganese Oxide .....	—
Magnesia .....	0.21
Lime .....	0.26
Potash .....	0.85
Soda .....	0.18
Loss .....	0.09

## ORDINARY SILICA BRICKWORK.

	per cent.
Silica .....	87.23
Titanic Oxide .....	1.85
Alumina .....	8.55
Ferrie Oxide .....	1.25
Manganese Oxide .....	—
Magnesia .....	0.10
Lime .....	0.28
Potash .....	0.54
Soda .....	0.36
Loss .....	0.25

H.M. Commercial Secretary at Copenhagen (Mr. Richard Turner, O.B.E.) reports that a well established local firm is desirous of setting up a permanent exhibition on behalf of ten or twelve United Kingdom firms manufacturing:

Scientific instruments.  
Surgical instruments.  
Cinematograph apparatus.  
Laboratory articles.  
X-Ray apparatus and tubes.  
Dentists' requisites.  
Surveying instruments.  
Drawing instruments.  
Polariscopes.  
Pyrometers and measuring instruments.  
Microscopes.  
Telescopes.

Further particulars regarding this proposition can be obtained by interested firms on application to the Department of Overseas Trade, 35, Old Queen Street, Westminster, S.W. 1.

### SAFEGUARDING OF INDUSTRIES ACT—PART I.

#### ARBITRATIONS UNDER SECTION 1, SUB-SECTION (5).

The Board of Trade have received formal notices of complaint under the above sub-section, that:

“Rochelle Salts” and  
Formaldehyde

have been improperly included in the lists of articles chargeable with duty under Part I. of this Act.

These complaints will be submitted in due course to the Referee appointed by the Lord Chancellor for the purposes of the sub-section, and any person interested should communicate immediately with the Assistant Secretary, Board of Trade (Industries and Manufactures Department), Great George Street, S.W. 1.

#### NORWAY'S FOREIGN TRADE.

The Commercial Secretary at Christiania has informed the Department of Overseas Trade that the statistics of Norwegian foreign trade, published by the Statistical Central Bureau, for the month of December, 1922, show the total of Norwegian exports during the past year to have amounted to 729.4 million kroner, and the re-export of foreign goods to 24.4 million kroner. Of Norwegian goods, paper to the value of 250 million kroner was exported, animal foodstuffs 167 millions, fertilisers, chemical products, etc. 76 millions, fats, oils, etc. 46 millions, and timber 76 millions.

During December, 1922, exports of Norwegian goods amounted to 57.5 million kroner, as compared with about 71 and 68 million kroner in November and October respectively.

#### CHEMICAL TRADE IN BRITISH MALAYA.

In common with other parts of the world, there has been a decided improvement in trade generally in the Malay Peninsula, the improvement being most marked in the latter half of last year. The following statistics dealing with supplies of chemicals, drugs, dyes, etc., for the Malay region clearly indicate this, and should be of interest to manufacturers and export merchants in this country.

The exports go mainly to Siam and the Siamese Malay States, Borneo, French Indo-China, and the Dutch Islands in the Archipelago. Acetic acid is extensively used for the coagulation of latex on the rubber estates of Malaya. In 1921, when the output of rubber was lower and other chemicals were being used, the total import of acetic acid amounted to 48,660 gallons, with an export of 24,699 gallons. Last year the import rose to 387,594 gallons, while only 30,964 gallons were exported.

#### IMPORTATION OF DYESTUFFS.

Dr. Attlee asked the President of the Board of Trade whether there was a scale for licences on the importation of dyestuffs under the Dyestuffs Act; and, if so, was the licence per pound based upon the colour or its quality, or was it purely arbitrary?

Viscount Wolmer replied: Section 2 (7) of the Dyestuffs (Import Regulation) Act, 1920, empowers the Board of Trade to charge in respect of each licence a fee not exceeding five pounds, to provide for the expenses of administration. The fees actually charged are on a sliding scale, based on the value of the consignment to which each licence relates, and range from 2s. 6d. on consignments of a value up to £100, to £5 on consignments exceeding £3,000 in value.

#### MORPHINE FACTORIES.

Cr. Bridgeman, the Home Secretary, informed Lord Robert Cecil that morphine factories were subject to inspection by the Home Office Inspectors under the Dangerous Drugs Act. Manufacturers were also required to keep detailed records, and make periodical returns, of their purchases

of the raw material, their production of the drug, and their sales, and a licence had to be obtained for each consignment of the drugs which was exported from this country. The Government were doing all that was in their power to check the abuses of the drug traffic, but until full international co-operation had been secured it would be impossible to prevent them altogether.

#### BIRMINGHAM SECTION OF THE INSTITUTE OF CHEMISTRY.

It has been decided to revive the Birmingham and Midlands Section of the Institute of Chemistry, which lapsed during the war. A provisional committee has been appointed, rules approved and submitted to the Council of the Institute for confirmation, and the following officers elected:—Chairman, Professor G. T. Morgan, Professor of Chemistry at the University; hon. treasurer, Dr. J. N. Friend, of the Birmingham Technical School; and hon. secretary, Mr. C. A. F. Hastilow.

It is intended to hold meetings of both a social and professional character, and to endeavour to promote co-operation and friendly intercourse between members of the chemist's profession.

Mr. R. B. Pileher (Registrar of the Institute) addressed a meeting recently of Fellows and Associates of the Institute of Chemistry in Birmingham.

#### CORRESPONDENCE.

##### THE AUTHENTICITY OF THE LATIN WORKS OF GEBER.

To the Editor of THE CHEMICAL NEWS.

SIR,—I was very interested in the account given in *The Chemical News* of Mr. Holmyard's lecture on "Arabian Alchemy and Chemistry."

It seems to be a matter of importance that as many of the Arabian alchemical MSS. as possible should be translated. These may add to our knowledge concerning the early history of chemistry, and settle the question as to whether the works attributed to Geber are to be regarded as those of Dschabir or not.

An English authority, Mr. H. S. Redgrove, in his *Alchemy*, p. 42 (second edition), inclines to Berthelot's view, as does also a German authority, Prof. E. O. von Lippmann, and recently, Dr. E. Darmstaedten has published a volume, entitled *Die Alchemie des Geber ubersetzt und erklart* (Berlin: J. Springer, 1922), in which he also distinguishes between Geber and Dschabir.

Among other points, he adduces that the Latin works are written in an obscure style, which would not have been the case if they were translations.

I regret I was unable to attend Mr. Holmyard's lecture, since it would be interesting to know upon what evidence he bases his conclusions that Berthelot was wrong in supposing these publications of Geber's to be spurious.—I am, yours etc.,

E. E. WHALE, B.Sc., F.C.S.

London, S.W.17.

#### NOTICES OF BOOKS.

*Handbook on Petroleum*, by CAPTAIN J. H. THOMSON and SIR BOVERTON REDWOOD. Fourth edition, revised and added to by MAJOR A. COOPER-KEY, C.B. Pp. XIX. + 342. London: Charles Griffin & Co., Ltd., Exeter Street, W.C.2. 1922. 12s. 6d. net.

The ever-increasing demand for petroleum and its products, and the consequent progress in all branches of the industry has necessitated the publication of this fourth revised edition of Thomson and Redwood's standard and comprehensive treatise on the subject.

Since the publication of the previous edition, technical science is the poorer by the death of Sir Boverton Redwood, and the present one has been revised and brought up-to-date by Major Cooper-Key. His special knowledge relating to such matters as transport, storage, questions of averting risks and dangers, and the official Acts, Orders and Regulations, is now made available for all in a form suitable for immediate reference.

The chapters originally compiled by Sir Boverton have undergone little alteration. As the old sources of petroleum oils will

gradually become inadequate to meet modern requirements, considerable skill and enterprise will be required to develop and exploit new fields.

This indispensable volume will continue to render most useful service to those engaged in any phase of the industry with which it deals.

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*A Method for the Identification of Pure Organic Compounds*, by SAMUEL P. MULLIKEN, PH.D. Vol. IV. Pp. VII. + 238. London: Chapman & Hall, 11, Henrietta Street, W.C.2. New York: John Wiley & Sons, Inc. 1922. 30s. net.

The chief portion of Prof. Mulliken's compendium is completed by the appearance of Vol. IV.

This has added fourteen "Orders" to the "Method," and has involved the tabulation of 3,900 additional specific characterisations to enable the identification of the more important organic compounds of these *Orders* when encountered in practical work.

Vol. I. of the *Method* provided for compounds of carbon, hydrogen and oxygen only; Vol. II. covered compounds containing nitrogen as well. Vol. III. was special, and contained descriptions of pre-war commercial dyes. Vol. IV. deals with the remaining classes of organic compounds, including halogen and sulphur derivatives, alone and with nitrogen bodies.

The sub-divisions are here extensive since all these elements are able to form wide series of *Orders*.

The rapid multiplication of known and applied organic substances and the introduction of better methods of classification necessitates careful revision from time to time, and it is anticipated that a supplementary volume will appear at an early date.

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*Dyes and their application to Textile Fabrics*, by A. J. HALL, B.Sc. (LOND.), F.I.C., F.C.S. Pp. 118. London: Sir Isaac Pitman & Sons, Ltd. 1922. 3s. net.

The subject of this little monograph has

received the attention of numerous writers during the past few years, but it is questionable whether the non-technical reader can obtain satisfaction from the extensive literature which already exists. The author has, therefore, made an attempt to interest general readers in this important industry, and we think he has succeeded. He has certainly written an excellent little book, in which he gives a delightful bird's-eye view of the whole of the industry devoted to the manufacture of dyestuffs and their application to various textile materials.

The first chapter gives an account of the development of the dye industry as it is to-day, and shows how it originated in the successful manufacture of coal gas from the work of William Murdoch at the commencement of the nineteenth century. It was not until fifty years after this event that Perkin produced the first synthetic dyestuff—Mauverne—by the use of the derivatives of products obtained from the tar product in the manufacture of coal gas—a bye-product previously considered as practically valueless and always a nuisance. Perkin's discovery had the immediate effect of directing the energy of chemists in this direction, so that to-day we have about a thousand differently constituted dyestuffs which are capable of serving the dyes in one way or another.

Chapters two and three are devoted to the nature of dyestuffs and their manufacture. To illustrate the kind of operations which go on inside a factory manufacturing synthetic dyestuffs, the manufacture of methylene blue is described. At the conclusion of this description the author draws the attention of the reader to the fact that, from his description of the difficulties which have to be solved before a single dyestuff can be manufactured, there is no cause for complaint against those who are endeavouring to establish a dye industry in this country when it is realised that over a thousand dyes have to be manufactured before dyers consider that they have an adequate range of colours.

Chapters four to ten are devoted to a description of the properties of the various textile fibres and the treatments to which they have to be submitted in order that they may acquire the pleasing effects which we have become accustomed to expect in the present-day manufactured textile fabrics.

In conclusion, this book contains numer-

ous excellent illustrations of the type of plant used in the industry. It is also provided with an index

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*The "Rapid" Decimal Calculator and Universal Reckoner*, by J. GALL INGLIS, F.R.S.E. London: Gall & Inglis, 31, Henrietta St., W.C.2. 1923. 1s. 6d. net.

Since a system of decimal coinage does not yet exist, it may be thought rather premature to publish a Rapid Decimal Calculator. But the publishers seem to view the matter with equanimity, and plunge into issuing a book of 80,000 calculations.

A glance at the leaflet accompanying the book indicates that it is neither more nor less than a gigantic multiplication table, with every unit up to 100 times 150; and the largest figure 504 times 1,050. The publishers also point out that foreign money exchanges, percentages, and even petrol consumption in miles per gallon can be easily found; while the multiplication table in itself will save calculating in square or cubic measures. This is the 77th reckoner issued by this firm.

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*Cements and Artificial Stones*, by the late JOHN WATSON, HON. M.A., F.G.S. Edited by R. H. RASTALL, Sc.D., M.Inst.M.M. Pp. XII. + 131. Cambridge, W. Heffer & Sons, Ltd. 1922. 6s. net.

The MSS. dealing with the specimens in the Sedgwick Museum, Cambridge, illustrating the economic geology of building materials, left by the late Mr. Watson, have now been published under the above title.

The volume is, however, more than a museum catalogue, but is not a textbook, since the author does not go deeply into the chemistry and physics of cement-making.

The historical development of this process is most interesting, and valuable information has been included by this method of treatment.

In the descriptive sections, specimens to

illustrate the raw materials, intermediate substances and finished cements and artificial stone. The specimens in the collection represent exclusively cements made in the British Isles. Acknowledgment is made to those firms who have contributed to the collection.

It is noticeable that most attention is now given to Portland cements, which are here described in greater detail. Others, including Roman and Sirapite cements, and Plaster of Paris, are also briefly described.

The bibliography at the end, and index, leave little to be desired.

The book certainly deserves the attention of economic Geologists, Architects, Chemical and other Engineers, and others concerned with the manufacture and uses of cement.

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H.M. Department of Scientific and Industrial Research has just issued a Second Report upon investigations conducted at the British Museum, entitled *The Cleaning and Restoration of Museum Exhibits*. Price 2s.

The continuation of Dr. Scott's researches has shown the urgent need for investigations of this kind. It is stated that the first report, issued in 1921, has led to numerous enquiries and requests for advice from museums, collectors, and even interested Continental firms. The latter, of course, fall outside the scope of these enquiries.

Especial importance will now be attached to these investigations in view of the recent discoveries in the tomb of King Tutankhamen.

It is a serious duty to succeeding generations to take adequate steps to preserve all collections of the tangible evidence of past phases in the life of mankind, and the appearance of this report should be widely welcomed.

The methods and reagents described must necessarily be used with care and discretion. Variations should only be introduced by experts possessing sound

scientific knowledge, and only after prior experiments have been made upon valueless objects.

Bulletin No. 8 (January, 1923) of the Bureau of Bio-Technology, has just been issued by Messrs. Murphy & Son, Ltd., thus completing the first volume, in which a number of practical contributions to technical biological science have appeared.

The first number of Vol. II. will appear in March, and will contain articles on the destruction of timber in mills, breweries, and other buildings, and its prevention; the suppression of insect pests and fungus diseases in relation to agriculture, malting, &c., micro-organisms in leather industries; and other matters of industrial importance.

#### BOOKS RECEIVED.

*Vat Colours*, by JOCELYN FIELD THORPE, C.B.E., D.Sc., &c., and CHRISTOPHER KELK INGOLD, D.Sc. Pp. XV. + 491. 1923. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 16s. net.

*The Rapid Decimal Calculator and Universal Reckoner*, by J. GALL INGLIS, F.R.S.E. 1923. Messrs. Gall and Inglis, 20, Bernard Terrace, Edinburgh. 1s. 6d. net.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

3348—Coley, H. E.—Manufacture of iron from iron ores. Feb. 5.

3727—Jackson, W. J.—Treatment of copper ores. Feb. 7.

3538—Koppers Co. — Treatment of ammonia-charged gas. Feb. 6.

3488—Plauson Parent Co.—Manufacture of emulsions of oleic acid, etc. Feb. 6.

3697—Soc. Chimique de la Grande-Paroisse.—Production of a nitrogen-hydrogen mixture for synthetic manufacture of ammonia. Feb. 7.

3476—Sundstrom, C.—Manufacture of a sodium compound. Feb. 6.

#### Specifications Published this Week.

192106—Marks, E. C. R. (Hoever Co.).—Process of recovering aluminium chloride used in the conversion of high boiling point hydrocarbons into low boiling point hydrocarbons.

192298—Boehringer Sohn, C. H.—Process for the preparation of papaverine nitrite.

192335—Pocock, L. D.—Fertilisers.

181719—Desmond, A., and Another.—Process for making Prussian blue starting from coal gas.

#### Abstract Published this Week.

190286—Barbituric acid compounds.—Jones, H., of 285, High Holborn, London.

The water-soluble calcium and magnesium salts of C-C-diethyl and C-C-phenylethylbarbituric acids are obtained by digesting a hot saturated solution of the acid with the theoretical quantity of freshly precipitated magnesium carbonate, which has not yet assumed the crystalline state, or of calcium or magnesium hydroxide, filtering the solution obtained and concentrating and drying in vacuo at as low a temperature as possible. An example shows the treatment with freshly precipitated magnesium hydroxide. It is post free for the official price of 1s. each. stated that the salts thus obtained are easily absorbable, and give permanent mixtures with the earth-alkali salts of acetylsalicylic acid.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on on post free for the official price of 1s. each.

#### SITUATION WANTED.

**A**NALYTICAL CHEMISTS (metallurgical preferred).—Gentleman with university training, desirous of experience and specialising, is willing to give his services as Junior Assistant Chemist for nominal consideration. Midlands preferred.—Address, A. L. Hues, 1, Castle Lane, Warwick.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3283.

## THE PROBLEM OF SUBSTITUTION IN THE BENZENE NUCLEUS AND THE THOMSON-LEWIS-LANGMUIR THEORY OF CO-VALENCE.

By RONALD FRASER AND JAMES ERNEST  
HUMPHRIES.

The work of the organic chemists who have directed their attention to the problem of substitution in the benzene nucleus falls naturally under two heads: speculation on the mechanism of substitution and the study of the directive influence of substituents already present in the nucleus. The present paper deals only with the second part of the problem, though it is realised that the two are probably interdependent, and the possible effect of addition preceding substitution has been kept constantly in view.

Modern theories, as exemplified by the ideas of Lapworth, Fry, Vorländer, Prins, and Flürscheim,\* agree in regarding orientation as occasioned by a differentiated condition—polarity or state of strain—of alternate carbon atoms. These theories inevitably bear among themselves a certain formal analogy, and the ideas here developed are no exception. They agree more particularly with those of Lapworth and Fry in possessing an electrical basis. Nothing is postulated, however, as to the constitution of the benzene nucleus, except that it is, of course, regarded as a six-membered ring; and we consider that the state of the molecule after the entry of a substituent and resulting from its presence is the important factor in orientation (*cf.*, Mills, *J. Soc. Chem. Ind.*, 1921, XL., 417, R., in his review of Fry's monograph).

\* The following references may be given to the papers of these authors: Lapworth, *Mem. Man. Phil. Soc.*, 1920, LXIV., ii., 1; *T.*, 1922, CXXI., 416; Fry, *The Electronic Conception of Valence and the Constitution of Benzene*, 1921; Vorländer, *Ber.*, 1919, LII. (B), 263; Prins, *Chem. Weckblad*, 1918, XV., 571; Flürscheim, *J. pr. Chem.*, 1902, LXVI., 321; *ibid.*, 1905, LXXI., 497.

We have taken as our basis the Thomson-Lewis-Langmuir theory of co-valence, and on this foundation have built up an electronic interpretation of Lapworth's Principle of Induced Alternate Polarities, as already elaborated by Kermack and Robinson (*T.*, 1922, CXXI., 427). We are not prepared at the present stage to differentiate between the relative sizes of the octets surrounding positive and negative centres, and for our present purpose this appears to be of secondary importance. The development of the theory is based on the following three postulates. In order to avoid the introduction of unnecessary synonyms, we shall adopt in the sequel the terminology used by Kermack and Robinson (*loc. cit.*).

*Postulate 1:* The tendency of a disintegrated octet is towards further disruption; and of a nearly completed octet towards completion.

*Postulate 2:* The tendency towards octet stability of an atom with nearly completed octet is greater than the tendency to octet instability of an atom with disruption only incipient.

*Postulate 3:* The more nearly a group approaches octet stability, the greater the ease of replacement at that point.

It will be observed that Postulate 2 is simply a statement in terms of octets of the conclusion arrived at by Briggs (*T.*, 1908, XCIII., 1564; *ibid.*, 1917, CXI., 253; *ibid.*, 1919, CXV., 278), viz., that negative fields are in general stronger than positive fields. Further, the relation of the carbon atom to Postulate 2 is of importance. It is generally recognised that carbon is unique in that it occupies the middle position in the first series of the periodic system, and is the first member of its group, containing the fewest number of electrons. It follows, then, that in a chain of carbon atoms of alternately positive and negative character, the positive centres tend to increasing negative character. Some interesting consequences of this element's electrical individuality will appear in the sequel.

Postulate 3 requires further discussion. We are of opinion that the distinction between polar and non-polar compounds is merely one of degree, and our views in this respect are those of Briggs (*T.*, 1921, CXIX., 1879), and of Kermack and Robinson (*loc. cit.*). The extreme case of octet stability is evinced in compounds which have come to be known as polar, where an



Fig. I., a, the octet of X tends to completion; hence the electrons shared with  $C_1$  are drawn into X, making  $C_1$  positive;  $C_2$  can now appropriate electrons shared with the unstable system  $C_1$ , acquiring negative polarity;  $C_3$  assumes positive polarity, and so on. In Fig. I., b, containing Y in a state of incipient disruption, the polarities are obviously as shown (*cf.*, Lapworth, *Mem. Man. Phil. Soc.*, 1920, LXIV., ii, 1).

A consideration of the figures will show that whatever is the cause of ortho-para substitution in Fig. I., a, will cause meta substitution in Fig. I., b. The elucidation of these causes involves a special consideration of the position of hydrogen with regard to octet stability. We regard the condition corresponding to octet stability of hydrogen as represented by the nucleus with no electrons.\* On this view, the hydrogen atom should be almost entirely lacking in a tendency to acquire an electron, and become the negative hydrogen postulated by Fry (*op. cit.*, pp. 20-27, p. 50). Our views receive strong support from the arguments of Stieglitz (*J. Amer. Chem. Soc.*, 1922, XLIV., 1293) against the existence of negative hydrogen in benzene compounds.

The main consideration seems to be rather the state of the carbon atom to which the hydrogen is attached. In a carbon atom of negative polarity, the octet is comparatively firmly held; hence the hydrogen attached to it is to a great extent deprived of its electron; the converse holding with a carbon atom of positive polarity. Bearing in mind the unique position of

† Attention should be directed at this point to the use of the terms positive and negative applied to the groups mentioned, in view of the fact that in discussions on orientation the terms are used, arbitrarily and in general, with the opposite meaning. This has already been noticed by Davies (*T.*, 1922, CXXI., footnote to p. 786). The same writer (*T.*, 1922, CXXI., 809) disproves the statement made by one of us (Fraser, *T.*, 1922, CXXI., 195) that the directive influence of substituents was partly dependent on their volume. The statement above is now preferred.

\* These remarks bring hydrogen (and the metals) into line with Postulate 2, which was stated in such a form as to make more obvious its application to the common organic elements, which lie to the right of the Periodic Table.

hydrogen with regard to octet stability, it is evident that the hydrogen nuclei attached to negative carbon atoms are in a

condition for ready substitution (Postulate 3).

Thus it is evident (Fig. I.) that the ortho-para hydrogens in Fig. I., a, are in a condition for ready substitution, while in (b) it is the meta hydrogens which are the more easily replaced. It is seen that the essential difference between the two types of substitution is brought out with exceptional clearness on this view; and, further, the ortho-para directive influence of X on the one hand, and the meta-directive influence of Y on the other, is as it should be, independent of the nature of the entering group.

The special reactivity of the hydrogen in the para-position to an ortho-para directive substituent follows immediately from the above considerations, inasmuch as (Fig. I., a), there is a reinforcing negative influence on the polarity of the 4-carbon atom.

#### ENTRY OF POSITIVE GROUPS.

It is well known that most of the radicles which can be introduced directly (*i.e.*, without the action of catalysts), into the benzene nucleus are positive (octet unstable). This follows at once from the preceding considerations. We have computed the number of electrons present in the typical positive radicles,  $\text{COOH}$ ,  $\text{SO}_3\text{H}$ , and  $\text{NO}_2$ , with the following results: (1)  $\text{COOH}$ , charge + 1, has sixteen electrons available for the formation of octets; adopting the Hantzsch-Lapworth structure for carboxyl, it is found that the carbon atom contains only six electrons in the sheath,

thus:  $\text{C} \begin{array}{c} \text{:}\ddot{\text{O}} \\ \text{:}\ddot{\text{O}} \\ \text{:}\ddot{\text{O}} \end{array} \text{H}$ . If the group replace a

hydrogen nucleus, the carboxyl carbon can readily complete its octet by sharing with the negative (octet stable) carbon atom in the nucleus, the octet of this atom being left complete by the removal of the hydrogen nucleus. (2)  $\text{SO}_3\text{H}$ . In sulphonation  $\text{H}_2\text{SO}_4$  reacts as  $\text{OH}^-$  and  $\text{SO}_3\text{H}^+$ ; on this basis, the  $\text{SO}_3\text{H}$  radicle contains twenty-four electrons available for octet formation.

This leads to the structure  $\text{H} \begin{array}{c} \text{:}\ddot{\text{O}} \\ \text{:}\ddot{\text{O}} \\ \text{:}\ddot{\text{O}} \end{array} \text{S} \begin{array}{c} \text{:}\ddot{\text{O}} \\ \text{:}\ddot{\text{O}} \\ \text{:}\ddot{\text{O}} \end{array}$

in which the sulphur atom contains only six electrons in the sheath. (3)  $\text{NO}_2$ . In nitration,  $\text{HNO}_3$  reacts as  $\text{OH}^-$  and  $\text{NO}_2$ ; on this basis the number of electrons in the  $\text{NO}_2$  radicle available for octet formation is

eighteen; this leads to the structure  $\text{N} \begin{array}{c} \text{:}\ddot{\text{O}} \\ \text{:}\ddot{\text{O}} \\ \text{:}\ddot{\text{O}} \end{array}$

in which the unstable centre, N, again con-

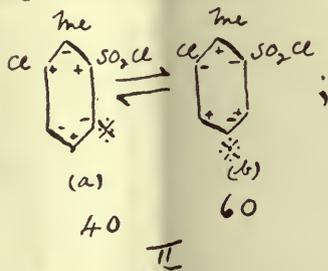
tains six electrons in the sheath. Similar arguments regarding the replacement of hydrogen apply to cases (2) and (3) as hold in (1).

It is clear that a negative (octet stable) substituent will not possess an electron content able to give the easy attainment of octet formation such as is possible in the cases cited above for positive substituents, and hence we should not expect the negative class to be so readily susceptible to direct introduction into the nucleus.

It is possible that we have here an underlying reason for the greater stability of compounds of the type (b) (see Fig. I. in last week's issue) than those of type (a) (Cf. Vorlander, *loc. cit.*).

#### THE HOLLEMANN SERIES.

The relation between octet stability and directive influence can now be discussed. Consider a typical case of a di-substituted derivative,  $C_6H_4XY$ , where the octet stability of X is greater than that of Y.

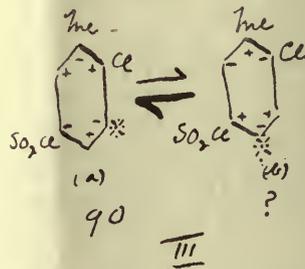


It follows from the relative stabilities of the octets of X and Y that the polarities of the carbon atoms should be as illustrated in Fig. II. (a) rather than that shown in II. (b). Generalising, it can be stated that the relative directive power of substituents follows a descending order of octet stability, and this seems to us to be the real implication of the Hollemann series.

Holleman (*Die direkte Einföhrung von Substituenten in den Benzolkern*, 1910, 466-469) points out that the directive tendencies of the commoner substituents follow the descending order: OH,  $NH_2$ , Cl, I, Br,  $CH_3$ , COOH,  $SO_3H$ ,  $NO_2$ . The tendency to octet stability doubtless follows the descending order:  $O > N > C$  (cf. Briggs, *Phil. Mag.*, 1921, vi., XLII., 449-450); this accounts for the position of OH,  $NH_2$ ,  $CH_3$ , it being remembered that the kernel octets are attached to positive hydrogen nuclei. The greater volumes of Cl, Br, I, agree with their comparatively low place in the series, increase in electropositeness with increase in volume being a well estab-

lished tendency which is readily interpreted electrically.\* (One would expect fluorine to be above hydroxyl in the series; next issue.) That all ortho-para directive substituents precede the meta follows from Postulate 2. Considering the meta-directive substituents among themselves, it is evident that electrons are more easily drawn from the labile carbon atom than from the more electropositive sulphur. The larger volume of sulphur as compared with nitrogen agrees with its high position, the effect of electropositeness being here opposite to that obtaining in the ortho-para directive series.

All possible cases of the entry of the third group into a disubstituted derivative will now be considered.



In the disubstituted compounds represented above,  $X_1$  and  $X_2$  are ortho-para directive (octet stable) substituents;  $Y_1$  and  $Y_2$  are meta directive (octet unstable) substituents.

Case 1: Fig. III., i. The induced polarities of the carbon atoms is as shown in (a) and (b), according as the influence of  $X_1$  or  $X_2$  predominates. Since the inductive effects are opposed, there will be an equilibrium between the two electromers, as indicated above.

The electromer present in greater concentration—a factor evidently determined by the relative octet stabilities of  $X_1$  and  $X_2$ —will react with greater velocity with the entering group; and the resulting trisubstituted compound will predominate in

\* The position of iodine relative to chlorine and bromine offers a curious anomaly. Owing to the differences of opinion existing with regard to the arrangement of electrons in the heavier atoms (Bohr, *NATURE*, 1921, CVII., 104; Bury, *J.A.C.S.*, 1921, XLIII., 1602), we have not attempted to account for it.

the final products. If  $X_1$  has the greater octet stability, further substitution will take place at the 4 and 6 positions; if  $X_2$ , at the 3 and 5 positions; *i.e.*, considered from the standpoint of  $X_1$  alone, ortho-para if  $X_1$  is negative and meta if  $X_1$  is positive. If the octet stabilities of  $X_1$  and  $X_2$  are widely different, one electromer may be present in such small concentration that its resultant will not be capable of detection in the final products. On the other hand, if the octet stabilities of  $X_1$  and  $X_2$  are of the same order, the number of products will be greater. The two possibilities may be illustrated by the iodination of *o*-toluidine (Wheeler and Liddle, *Amer. Chem. J.*, 1909, XLII., 501), and the nitration of *o*-chlorotoluene (Wibaut, *Rec. Trav. Chim.*, 1913, XXXII., 244).

Similar reasoning applies to disubstituted derivatives of the type  $C_6H_4 X_{1(1)} X_{1(4)}$

Case 2, Fig. III., ii. In this case the octet tendencies of  $X_1$  and  $X_2$  reinforce each other, and a single electromer exists. Substitution would be expected to occur at the 4 and 6 positions, which is in agreement with the facts.

Case 3. This is similar to Case 1. If the octet instability of  $Y_1$  is greater than that of  $Y_2$ , electromer (a) will predominate, and if conversely, electromer (b). Further substitution will proceed accordingly.

The type  $C_6H_4 Y_{1(1)} Y_{2(4)}$  is similar.

Case 4. A single electromer. Further substitution at 5.

Case 5. A single electromer. The groups X and Y reinforce each other's natural octet tendency. The smooth nitration of the nitrophenols is all in agreement with this statement. The type  $C_6H_5 X_{(1)} Y_{(4)}$  falls under this case.

Case 6. Equilibrium between electromers holds in this case; reference to Postulate 2 indicates that the direction of equilibrium will be that shown (Fig. III., vi.), and hence ortho-para directive substituents will exert the greater influence in orientation.

#### THE EFFECT OF CONDITIONS.

One of the main difficulties to the formulation of definite rules summarising the facts of orientation is the effect of conditions in altering the relative amounts of the final products of a reaction. On the octet view, this means that the equilibrium pictured above in the electromeric equations, or, in the cases where a single elec-

tromer exists, the relative octet stabilities of the substituents, is altered. In either instance, this would indicate that the effect of conditions is largely one of electron transference.

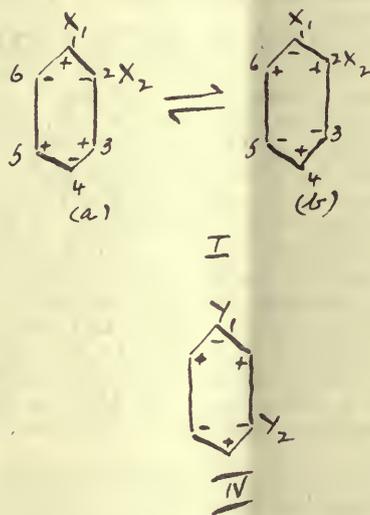
The work of Biltz (*Z. Elek.*, 1911, XVII., 676) has shown that carbon possesses a very high characteristic vibration frequency; and, as stated by W. C. McC. Lewis (*System of Physical Chemistry*, vol. III., 62), "an atom possessing high frequency is no doubt the most likely type of atom to allow of the transference of electrons to and from itself." That electron energy increases with rise of temperature has been indicated by Koenigsberger (*Z. Elek.*, 1911, XVII., 289), and electron lability must also be affected by the nature of the solvent medium (dielectric constant, etc.). It is along these lines that we hope to approach the problem of conditions.

#### REPLACEMENTS AND OCTET STABILITY.

The term "Replacement" is used to denote the exchange of one substituent for another; "Substitution" refers to the exchange of hydrogen for an entering group. It seems to us that no essential distinction can be drawn between the two processes; and we regard substitution merely as a special case of replacement. No rule of replacement corresponding to a rule of substitution has, so far as we can find, been formulated; but consideration of our remarks on the special case of the "octet stability" of hydrogen appears to lead to some degree of uniformity in this respect. It was pointed out that the lability of hydrogen was conditioned by its tendency to give up its electrons; whereas octet completion is the determining factor in the lability of all other elements attached to the nucleus. In other words, a labile hydrogen is attached to a negative carbon atom, while a labile radicle other than hydrogen is attached to a positive carbon.

Thus, any rule which expresses the facts of substitution will be reversed in the case of replacement; by "reversed" we mean that a group which causes *substitution* in the meta position will favour *replacement* in the ortho-para positions, and conversely. For example, the nitro group causes substitution in the meta position; but in the hydrolysis of the nitranilines, replacement of  $NH_2$  by OH occurs at the ortho-para positions to the nitro group, and not at the meta position. Reasoning on the same lines as

those employed in the discussion of substitution, it will be seen (Fig. IV., a and b),



that the octet stability of  $\text{NH}_2$  is reinforced by the polarity effects of the nitro group: whereas in Fig. IV. (c), the polar tendencies of  $\text{NH}_2$  and  $\text{NO}_2$  are opposed, and the lability of  $\text{NH}_2$  consequently diminished.† We have found the above rule (which is, of course, the obverse of the Brown and Gibson rule) to be of general application to the simpler cases.

Another interesting rule follows from the unique electrical character of the carbon atom discussed above, if we enquire how the tendency there mentioned towards increasing differentiation of polarity in a chain of carbon

\* A ringed group, thus (x), is used here to denote lability following on octet stability.

† Reference to Case VI. shows that nitraniline exists as two electromers, the  $\text{NH}_2$  group exerting the greater directive influence. It would appear that the lability of a group is more easily influenced by one of opposite polar tendency than is its directive influence; and this is in general agreement with our views on reactivity. In this connection it should be noted that the  $\text{NH}_2$  group in aniline itself, while exerting full directive power, requires the reinforcement of ortho or para nitro groups to render it labile in hydrolysis; and many other similar instances could be cited.

atoms can be satisfied.‡ The inductive effect of a substituent on the carbon atoms of the nucleus is greater the greater its octet stability (*cf.* discussion of the Hollemann Series); hence the differentiation of polarity of the carbon atoms will be increased by the replacement of the given substituent by a group of greater octet stability. The rule may therefore be stated thus; in replacements, the entering group is one of greater octet stability than the group replaced. The hydrolysis of the nitranilines is a case in point, and many others have been examined, and the rule found to hold.\*

A striking example of the application of the rule is seen in the recent work of Swarts (*Bull. Acad. roy. Belg.*, 1920, 389) on the nature of the  $\text{CF}_3$  group.  $\text{CF}_3$  is, as one would expect, meta directive. Unlike  $\text{C}_6\text{H}_5\text{CCl}_3$ ,  $\text{C}_6\text{H}_5\text{CF}_3$  can be nitrated under ordinary conditions without hydrolysis of the  $\text{CF}_3$  group. This is pre-looked for, replacement of F by OH is, according to the rule, difficult or impossible.

Hitherto the application of the rule has been confined to the entry of groups of an essentially electronegative character; but we have found that the important class of reduction reactions, where a group is replaced by hydrogen, falls equally under the rule. In a recent series of papers, Mac-

‡ The rules of Michael and Markownikoff may be a consequence of this property of a chain of carbon atoms, the inductive effects being more pronounced when the chain is unsaturated (Kermack and Robinson, *loc. cit.*, pp. 430-432). In the examples  $\text{CH}_2\text{CH}:\text{COOH} + \text{HBr} = \text{BrCH}_2\text{CH}_2\text{COOH}$ ; and  $\text{CH}_3\text{CBr}:\text{CH}_2 + \text{HBr} = \text{CH}_3\text{CBr}_2\text{CH}_3$ , the reaction has taken place which increases the polarity (positive or negative) of the carbon atoms.

\* An apparent exception to the rule is the action of  $\text{PCl}_5$  on phenols, where OH is replaced by Cl. The chlorines in  $\text{PCl}_5$ , however, may be in an exceptional state of octet stability (*cf.* Thomson, *Phil. Mag.*, 1921, [vi.], XLII., 521). It is in agreement with the deductions on p. 16 that the reaction takes place more readily with *p*-nitrophenol than with phenol itself.

cisely what we should expect on the octet view. It was pointed out (see last week's issue) that fluorine was in all probability more octet stable than any other atom or group; therefore, while the replacement of Cl by the more octet stable OH group is to

beth and his co-workers (Henderson and Macbeth, *T.*, 1922, CXXI., 892; Hirst and Macbeth, *ibid.*, p. 904; Macbeth, *ibid.*, p. 1116) have pointed out that, different as are the structures of compounds with halogens labile towards reducing agents, they have in common the possession of halogen with a strong induced positive polarity—that is, on our view, octet unstable. The octet instability in the cases cited by these authors appears to be unusually pronounced, and hence their ready replacement by negative (octet stable) groups is not to be expected. Their replacement by hydrogen, however, which tends to become electropositive and "octet stable" at the same time (*vide supra*), is in agreement with the rule and with its underlying foundation, viz., *the tendency towards increasing differentiation of polarity of the carbon atoms*. The replacement of the halogen by

It is important to note here the finding of Burton and Kenner (*T.*, 1922, CXXI., 675), that in the removal of halogen in the reduction of halogenated nitro-compounds, the reduction of the nitro groups to amino groups in all probability precedes the removal of the halogen (*cf.* the examples cited by Burton and Kenner, *loc. cit.*, and the papers of Macbeth and his co-workers mentioned above). The present theory would predict that such is the course of these reactions.

#### EFFECT OF GROUPS ON EACH OTHERS REACTIVITY.

We can now refer more particularly to the loosening or tightening effects on substituents caused by other groups present in the nucleus, as has been referred to already in the simpler cases (Fig. IV.). Among the numerous examples examined, may be cited the following: the loosening effect of meta directive groups on substituents in the ortho-para positions (Schopf and his collaborators, *Ber.*, 1889, XXII., 900, *et seq.*; Kenner, *loc. cit.*); the loosening of ortho-para directive groups on substituents in the meta position (Kenner and Parkin, *T.*, 1920, CXVII., 855; Hollemann and metals in this class of compound (Henderson and Macbeth, *loc. cit.* p. 895) is a similar example of the rule.\*

\* *The activity or inertness of halogen in the compounds cited by Kenner (T., 1914, CV., 2719) and explained by him on Flürscheim's formulation, can be equally well interpreted, along the above lines, on our views.*

Hollander, *Rec. trav. chim.*, 1920, XXXIX., 435; Guia, *Gazzetta*, 1921, LI., i., 307; Burton and Kenner, *T.*, 1922, CXXI., 489); the tightening effect of ortho-para directive groups on bromine in the para position (Meyer, *Ber.*, 1921, LIV., [B], 2265). An examination of these will show that our views, and in particular Postulate 3, are capable of predicting the observed facts.

#### THE DIRECTING GROUP IN POLYSUBSTITUTED COMPOUNDS.

In a large number of cases examined by Robinson (Perkin and Robinson, *T.*, 1914, CV., 2379; Jones and Robinson, *T.*, 1917, CXI., 906; Gibson, Simonsen, and Rau, *T.*, 1917, CXI., 73), it is found that when a negative group is in the ortho-para position to a positive group, they neutralise each other, and the orientating effect is exercised by the second positive group. The work of Davies on the cumulative effect of the chlorine atom and the methyl and sulphonyl chloride groups on substitution (Davies, *T.*, 1921, CXIX., 853-876; *ibid.*, 1922, CXXI., 785) affords interesting examples of the applicability and otherwise of the Robinson rule.

In attempting to determine the position taken up by a fourth substituent in a tri-substituted derivative, two main considerations are of importance, viz., the relative octet stabilities of substituents already present, and the persistence of their inductive effects through a chain of carbon atoms.



Percentage yield of corresponding nitro compounds (substitution at asterisk). The substances on which Davies worked

(Fig. V.) contain in each case  $\text{CH}_3$  and Cl in the ortho relation, the  $\text{SO}_2\text{Cl}$  occupying various positions relative to them. The octet stability of Cl being greater than that of  $\text{CH}_3$ , the predominating polar state of the molecule, in the absence of the  $\text{SO}_2\text{Cl}$  group would be as indicated in Fig. V., ia, iia, iia. Consider now the question of the persistence of induction. In Fig. 5 i., the inductive tendency of Cl in reversing the natural polarity of  $\text{SO}_2\text{Cl}$  is greater than that of  $\text{CH}_3$ , which has the opposite tendency, owing to the difference in the number of carbon atoms through which induction has to be effected. On the other hand, in Fig. 5 ii., the greater inductive power of Cl as compared with  $\text{CH}_3$  is balanced by the weakening effect of the carbon atoms intervening between Cl and  $\text{SO}_2\text{Cl}$ .\* In Fig. 5 iii., the  $\text{SO}_2\text{Cl}$  and Cl have the same polar effects on the nuclear atoms. The electromeric equilibria in the three cases will therefore be as shown in that figure, and the yields of the nitration products are in agreement. Thus it will be seen that the present theory is borne out by the above experiments; whereas the Robinson rule fails in the third example (v., Davies, *T.*, 1922, CXXI., 786; but compare footnote to same page).

The results of Gibson, Simonsen, and Rau (*T.*, 1917, CXI., 69) on the nitration of 2-acetylamino-3-4-dimethoxybenzoic acid and of 3-acetylamino-veratrole, and of Simonsen and Rau (*T.*, 1917 CXI., 220) on the nitration of isomeric acetylamino methoxybenzoic acids, are difficult of interpretation on the octet view, partly owing to the large number of substituents, and hence the difficulty of determining their mutual interdependence; and partly to the difficulty at the present stage of dogmatising with regard to the relative octet stabilities of  $\text{NHAc}$  and  $\text{OMe}$ .

In the above, we have attempted, on the basis of the Thomson-Lewis-Langmuir theory of co-valence, to connect various

\* Morgan and Jones (*T.*, 1921, CXIX., 187) on nitrating 2-chloro 6-nitrotoluene, obtained 90 per cent. of the compound corresponding to iia above, and 5-10 per cent. of iib. Reference to remarks on the order of the meta directive substituents indicates that electromer (x) can exist in greater concentration when an  $\text{NO}_2$  group is in place of  $\text{SO}_2\text{Cl}$ .

theories and rules which at first sight may seem wide apart; to give as consistent a basis as we could to certain observed regularities; and further, to formulate generalisations which may be of use in classifying, and perhaps in predicting the course of, substitution reactions.

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#### GENERAL MEETING OF THE CO-OPERATORS IN THE BRITISH CHEMICAL STANDARDS' MOVEMENT.

*(Standard Analysed Samples of Iron, Steel, Etc.)*

On February 9, at York, a "Report on the Second Three Years' Working" (ending Sept. 30th, 1922) was read, and details of the work during this period were given. A list was given of 53 analysts who had taken part in the standardisation, and 20 firms, who had provided material. Ten new samples comprising 46 actual standards were described. Reference was made to the outstanding events since the commencement, and a chronological list of standards—including the total weights standardised—was shown; and copies of the 32 certificates issued (from the earliest onwards). British, French, and Italian price lists, and diagrams illustrating the preparation of the standards, were exhibited. The extreme precautions taken to ensure perfect homogeneity were described. No allegation as to, or evidence of, lack of homogeneity of the standards was elicited. In view of their wide adoption, every means was used to meet even theoretical difficulties, to warrant the confidence of users.

A sample of shavings of the latest standard, "C," was shown, illustrating their extreme thinness and suitability for direct combustion carbon determination. A single portion of usual weight averaged 1,700 pieces with 90 sq. ins. superficial area.

Within six years the movement had steadily developed and become consolidated, maintaining its progress, in spite of the many adverse conditions of recent years. Commencing with a few co-operators in a few localities, their number and range of interests had multiplied many



times, and now included members from several countries, some 15 to 20 co-operators taking part in each standardisation. The 23 samples produced, comprising 83 standardised results, had covered practically the whole range of plain carbon steels in regular use, and included four alloy steels as well as two cast irons and a basic slag. The weight per standard had risen to twenty or twenty-five times, and the available duration, permanency, and value for reference, had increased proportionately; yet the quality, homogeneity, and fine state of turnings, etc., had not merely been maintained, but improved. Many large works' laboratories used these standards, and their use had so spread that sole agents had been appointed in Italy and France. The 450 British and foreign users included 10 Government Departments, 30 universities and technical schools, and 5 railways.

This progress had fully justified the policy adopted; the organisers, whilst having had the advice and general guidance of the co-operators, had also freedom of action in detail.

The organisation was not restricted to any one society or industry, and was not dependent on the same group for standards for which it might not be fitted. For each type, co-operators recognised as experienced specialists in that class of analysis were selected.

Their work had demonstrated that in analysis *divergencies* occurred to an *unrealised degree* on every sample tested, even under the most favourable conditions of homogeneity and careful working.

*Jointly standardised samples* were a *necessity* to reveal these *divergencies* and clear them up.

*The rapid development of their movement* and consequent *creation of such standardised samples for certain types of material* was the *surest way to analytical co-ordination*—which desideratum not only vitally affected the value and status of chemists, but *gave the maker a definite gauge* by which to attune his manufacture, *secure for the engineer or user closer adherence to specification*, and *save many delays in delivery*, and *disputes* which now occurred.

Their organisation provided *practical working machinery* for the production and distribution of standards, and they were justified in believing that the same methods used for iron and steel standards could be

applied with equal efficiency to *other materials*.

A thorough and interesting discussion followed.

A series of iron and steel standards now existed, which covered the needs of engineers, users, and makers fairly completely, and it was now for these to make full use of them, so that the movement's objects could be achieved. Co-operators had offered to arrange meetings to explain the objects of the movement and uses of the standards. Anyone interested could be invited.

Resolutions were passed: (1) Approving of the general conduct of affairs by the organisers and adopting their report; (2) thanking the Committee for their assistance in the past and reappointing them with two others, to act in all matters where it might not be considered necessary to consult the whole body.

(3) "That we, as co-operators in the British Chemical Standards' Movement, recommend that the fullest use should be made of standard analysed samples of steel, iron, and other substances, particularly in the following ways:—

(a) By *engineers*, in their chemical specifications, referring regularly to some *specific* standard sample of *similar type*, and requiring that in cases of dispute, a check analysis of it shall be made concurrently by the reference chemist, as a gauge of the values found.

(b) By *chemists* (a) using them periodically for checking and co-ordinating their routine tests, and (b) invariably as an aid to settling disputes, (c) stating on their reports that such standards have been used."

"We would recommend *any suitable standards*, prepared on a *sufficiently wide basis*, for acceptance by those between whom disputes may arise, and obtainable by all parties (for example)—so far as any or all of them conform to this—those prepared by the United States Bureau of Standards, those prepared jointly by the Iron and Steel Institute and National Physical Laboratory, or our own series of British Chemical Standards which are already in use in about 450 laboratories in Great Britain, the Colonies, and other countries;

"And further, we recommend that a copy of this resolution be sent to engineering and chemical societies, and that they be earnestly requested to consider the im-

portance of bringing before their members the scientific and practical value of chemical standards."

The fourth resolution bore on the limits of accuracy of analytical methods.

It was resolved, in view of the importance of figures with which it should be coupled, that the Committee should obtain supplementary data and submit this with the resolution to the whole body of co-operators and to such other persons as they might think desirable.

The fifth resolution appointed a Committee to consider the question of forming on a financial basis a more formal organisation, with separate official headquarters, and to report to the co-operators.

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### GENERAL NOTES.

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#### AUSTRIA'S FOREIGN TRADE IN 1922.

The Commercial Secretary at Vienna (Mr. O. S. Phillpotts) has forwarded a report on the foreign trade of Austria for 1922.

In 1922 there was a large reduction in the value of the imports, and a still larger increase in that of the exports. Consequently, there is an important diminution in the excessive adverse balance of trade from which this country has suffered since the war.

Exports of wood, magnesite, and manufactured goods generally, showed a large increase. The value amounted to 900 million gold crowns (£35.4 millions), or 86 per cent. of all the exports. There were also important increases in cotton goods, made up clothing, paper and paper goods, rubber goods, wooden goods, cement, and iron and metal goods. The export of machinery declined, and although the quantity of leather and leather goods was greater. Of the imports into Austria, Germany sent 37.7 per cent., Czecho-Slovakia 37.1 per cent., Hungary 6.3 per cent., Poland 5.5 per cent. No other country sent more than 2 per cent. The share of the United Kingdom was only 0.6 per cent., but it does not send to Austria much of the bulky and heavy articles such as fuel and foodstuffs. According to British official statistics, the value of the produce and manufactures from the United Kingdom was £1,308,238.

This is considerably less than the figure for 1921, £1,734,000, but is much larger than the British imports into the Succession States, Czecho-Slovakia, Hungary, and Yugoslavia, where the import of British goods declined during the year in about the same proportion.

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#### CALCIUM ARSENATE AND WHITE ARSENIC FOR THE UNITED STATES.

The Commercial Counsellor at Washington reports that certain firms in Savannah are desirous of receiving quotations from United Kingdom firms for the supply of calcium arsenate and white arsenic.

The names and addresses of the firms in question, together with further particulars on the subject, may be obtained by U.K. firms interested upon application to the Department of Overseas Trade, 35, Old Queen Street, S.W.

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#### BARIMAR MOVE TO LARGER PREMISES.

To keep pace with the enormous growth of their scientific welding business, Barimar, Ltd., have moved to larger and more commodious London premises at 14/18, Lamb's Conduit Street, Theobalds Road, London, W.C.1. While Barimar, Ltd., make this move from their old premises with considerable reluctance, they feel that they will be serving the interests of their customers best by operating a larger factory with the offices on the spot, and so speed up delivery of repaired parts and be free to handle a greater volume of work under the best conditions. The Barimar Service Depots at Birmingham, Manchester, Leeds, Newcastle-on-Tyne, Cardiff and Glasgow will continue to repair scored cylinders by their metallurgical (patented) process, and to deal with welding and repair work as hitherto.

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#### PROCEEDINGS AND NOTICES OF SOCIETIES.

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##### THE ROYAL SOCIETY.

THURSDAY, MARCH 8, 1923.

Papers read:—

A. B. WOOD, H. E. BROWNE and C. COCHRANE. *Determination of Velocity of Explosion-Waves in Sea Water. Variation*

of Velocity with Temperature. Communicated by F. E. Smith, F.R.S.

P. M. S. BLACKETT. *The Study of Forked Alpha-ray Tracks*. Communicated by Sir Ernest Rutherford, F.R.S.

The methods described in a former paper were applied to the study of the forked alpha-ray tracks obtained by the Wilson condensation method.

Measurements of the lengths of the tracks of the recoil atoms yielded information concerning the relative ionisation due to different kinds of ionising particles, and of the average charge carried by them.

Special methods were developed for obtaining accurate measurements of the angles between different parts of the tracks. Application of this was made to the determination of the masses of the recoil atoms in three particularly favourable cases. These measurements gave values, within the limits of the probable error, in agreement with those to be expected from the composition of the gas.

A. EGERTON. *On the Vapour Pressure of Lead. I*. Communicated by Prof. F. A. Lindemann, F.R.S.

The vapour pressure of lead is measured by effusion of vapour at low pressure through a hole of measured area. Temperature is maintained constant by a selenium cell relay arrangement within  $1/3^{\circ}$  C. for many hours at temperature about  $800^{\circ}$  C. Pressures have been measured to  $10^{-5}$  mm. The vapour pressure of ordinary lead between 1,200-600° absolute is expressed by the equation

$$\log p = 7.908 - \frac{9932}{T}$$

An attempt has been made to determine the difference of vapour pressure of lead and the uranium-lead isotope; the experiments lead to a difference of 2 per cent., but the result is rendered uncertain by an unexplained lowering of vapour pressure which lead undergoes on prolonged heating *in vacuo*.

A. C. EGERTON and W. B. LEE. *Some Density Determinations*. Communicated by Prof. F. A. Lindemann, F.R.S.

The Archimedes method of determining densities is rendered more accurate by utilising certain mobile and heavy organic liquids which avoid air bubbles and damping difficulties, and increase the weight of liquid displaced. The suspension difficulty is also overcome.

The density and boiling points of the liquids employed—ethylene dibromide and carbon tetrachloride—have been determined with accuracy. Density determinations are discussed and a differential method suggested.

The preparation of a satisfactory sample of metal for density determination is rendered possible by filtering, casting and heating *in vacuo*.

The density of lead is determined, viz., 11.3437 at  $20^{\circ}$  C. The probable error of the nine determinations on three different samples of metal is 1 part in 100,000. The maximum departure from the mean value for any single determination is less than 1 part in 12,000.

The density of a sample of uranium-lead is checked, and would have an atomic weight of 206.26 from the density obtained.

Determinations of the density of a small sample of cadmium of 1.5 grams weight agree to 1 part in 20,000.

A. C. EGERTON and W. B. LEE. *Separation of Isotopes of Zinc*. Communicated by Prof. F. A. Lindemann, F.R.S.

Two sets of distillations of pure zinc have been carried out in high vacuum, under conditions to obtain a slightly different concentration of the isotopes in the final residue of the final distillate. The conditions under which the samples are prepared for density determinations are described. The samples are cast *in vacuo* and seeded with a particular kind of zinc.

The measurements of density are carried out by the method described in the preceding paper, with improvements to the apparatus.

The first set of distillations gave a residue of slightly increased density, but the distillate possessed the same density as the original zinc. The second set of distillations gave a residue of increased density (about 1 part in 3,700) and a distillate of decreased density (about 1 part in 3,000). Determinations on seven samples of ordinary zinc agree in giving the density of zinc (prepared in the described way) as 7.1400 (the probable error being less than 1 part in 100,000).

Flaws, allotropes, different physical conditions, and impurities as explanations of the result are shown to be improbable. The result lies outside the experimental error.

The amount of the separation agrees with Dempster's observations of isotopes of weights extending over six units (viz.,

34-70), but is not as great as might be found for equal parts of 64 and of atoms of weights 66, 68 and 70.

E. HATSCHEK and P. C. I. THORNE. *Metal Sols in Non-dissociating Liquids. I.—Nickel in Toluene and Benzene.* Communicated by Prof. A. W. Porter, F.R.S.

The results obtained so far may be summarised as follows:—

Very stable sols of nickel in a medium free from ions can be produced by decomposing nickel carbonyl dissolved in mixtures of toluene and benzene, containing a small amount of rubber, at 100° C.

In the electric field the particles of disperse phase move to, and deposit on, both electrodes.

Electrophoresis in fields of different strengths, all other factors being equal, shows that the amounts deposited are proportional to the first, or a lower, power of the potential gradient. The charges, therefore, are not induced ones, but positively and negatively charged particles are originally present in the sol.

The sol resembles typical protected aqueous sols, inasmuch as it is coagulated by liquids which are not solvents for the protective colloid, *i.e.*, rubber. The coagulum is only very imperfectly peptized again by rubber solvents, such as toluene or benzene.

Paper read in title only:—

H. HIRATA. *Constitution of the X-ray Spectra belonging to the L Series of the Elements.* Communicated by Sir William Bragg, F.R.S.

THURSDAY, MARCH 15, 1923.

Papers read:—

G. C. STEWARD. *Aberration Diffraction Effects.* Communicated by Prof. A. S. Eddington, F.R.S.

Papers read in title only:—

LORD RAYLEIGH, F.R.S. *Further Observations on the Spectrum of the Night Sky.*

LORD RAYLEIGH, F.R.S. *Studies of iridescent Colour, and the Structure producing it. IV.—Iridescent Beetles.*

PROF. J. W. NICHOLSON, F.R.S. *Oblate Spheroidal Harmonics and their Applications.*

PROF. J. W. NICHOLSON, F.R.S., and PROF. F. J. CHESHIRE. *On the Theory and Testing of Right-angled Prisms.*

PROF. J. C. McLENNAN, F.R.S., and D.

S. AINSLIE. *On the Fluorescence and Channeled Absorption Spectra of Caesium and other Alkali Elements.*

W. STILES, Sc.D. *The Indicator Method for the Determination of Coefficients of Diffusion in Gels, with special reference to the Diffusion of Chlorides.* Communicated by W. B. Hardy, Sec. R.S.

H. T. FLINT. *A Generalised Vector Analysis of Four Dimensions.* Communicated by Prof. O. W. Richardson, F.R.S.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

On Saturday, March 17, SIR ERNEST RUTHERFORD, LL.D., D.Sc., F.R.S., will give his fifth lecture on *Atomic Projectiles and their Properties*, dealing with the life history of an  $\alpha$ -particle from radium.

On March 13, PROF. C. G. SELIGMAN delivered the first of two lectures at the Royal Institution, on *Rainmakers and Divine Kings of the Nile Valley*; and on March 15, COLONEL E. F. STRANGE began a course of two lectures on *Japanese and Chinese Lacquer*.

#### THE CHEMICAL SOCIETY.

ORDINARY SCIENTIFIC MEETING, THURSDAY, MARCH 15, 1923.

The following papers were read:—

*The oxime of mesoxamide (isonitrosomalonalamide) and some allied compounds. Part III.—Ring formation in the tetra-substituted series.* E. H. USHERWOOD and M. A. WHITLEY.

*The preparation and stability of cuprous nitrate and other cuprous salts in the presence of nitrites.* H. H. MORGAN.

*The interaction of hydrogen sulphide, thiocyanogen and thiocyanic acid with unsaturated compounds.* F. CHALLENGER, A. L. SMITH, and F. J. PATON.

*The polarity of double bonds.* T. M. LOWRY.

#### INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The Tenth Annual General Meeting was held at the House of The Royal Society of Arts, John Street, Adelphi, on March 13. PROF. J. S. S. BRAME, F.I.C., F.C.S., the retiring President, gave an address.

### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

At the Ordinary Meeting, held at the Chemical Society's Rooms on March 7, Mr. P. A. Ellis Richards, President, in the chair, certificates were read for the first time in favour of: Mr. John Myers, F.I.C., and John Loudon Buchanan, F.I.C.

Certificates were read for the second time in favour of: Messrs. Joseph John V. Baikes, A.R.C.Sc., A.I.C., D.I.C., Samuel Gordon Stevenson, A.I.C., Laurence Barnett Timmis, M.Sc.Tech. (Manch.), A.I.C., Richard William Sutton, B.Sc.-Tech. (Manch.), A.I.C., Alfred Edward Johnson, B.Sc. (Lond.), F.I.C., A.R.C.S.I., Ernest Victor Jones, F.I.C., Francis Kenelm Donovan, S. Gordon Liversedge, F.I.C.

The following were elected members of the Society: Messrs. George Henry Appleyard, F.I.C., Arthur William Starey, A.R.C.S., B.Sc. (Lond.), A.I.C., John Matthew Wilkie, B.Sc. (Lond.), F.I.C.

The following are abstracts of the papers communicated:—

*The Examination of Firearms and Projectiles*, by A. LUCAS, O.B.E., F.I.C.

The scientific methods used for the identification of firearms and projectiles in cases of wounds or deaths from shooting were discussed. It was shown that a particular weapon may sometimes be recognised by the rifling marks imprinted on a bullet, and that the nature of the fouling left in the barrel after the weapon has been fired may also afford valuable information both as to the nature of the original powder and also, in some cases, the period that has elapsed since the last discharge. The composition, dimensions, and markings on bullets, slugs, etc., were described, and directions were given for the reproduction of rifling marks on bullets, and for the chemical analysis of projectiles of all kinds.

*The Interpretation of the Results obtained in the Analysis of Potable Waters*, by ROBERT C. FREDERICK.

This is an account of an extended investigation into the chemical changes which occur in samples of excretally polluted water. The findings are considered in conjunction with the results obtained by the author in the analysis of a very large number of samples from every kind of supply throughout the British Isles. The orthodox ideas in regard to the interpretation of the analytical results of such examinations

are criticised and the author's own views detailed.

*Determination of the Purity of Vanillin*, by SYDNEY B. PHILLIPS, A.I.C.

After reviewing the various methods proposed from time to time, the author described two processes for estimating vanillin. The first was a volumetric one, where 1 gram of vanillin is dissolved in 20 cc. of neutral alcohol, and acid impurities are neutralised. 1.2 grams of *p*-toluidine are then added, and 20 cc. of semi-normal sodium hydroxide solution are measured in, followed by 100 cc. of cold water. The solution at 15° C. is titrated with semi-normal sulphuric acid until the permanent precipitate of the condensation product of vanillin and *p*-toluidine is formed. The difference between the volumes of alkali and acid represents the volume of alkali required to combine with the vanillin.

A summary of the gravimetric method is as follows:—One gram of vanillin is dissolved in 13.6 cc. of semi-normal sodium hydroxide. To this is added a solution of 2.4 grams semi-carbazide hydrochloride and 3 grams of anhydrous sodium acetate, or 5 grams of the crystalline salt in 30 cc. of water. The mixture is heated on a boiling water bath for 10 minutes, allowed to stand in the cold for four hours, and the semi-carbazone filtered off, washed, dried, and weighed. It is treated with ammonium hydroxide solution, and the insoluble portion filtered off, washed, dried, and weighed. This weight is deducted from the original weight of semi-carbazone, and the remainder calculated to vanillin.

### MINERALOGICAL SOCIETY.

The following papers were communicated on March 13:—

A. HUTCHINSON. *A Graphical Method of Correcting Specific Gravity Determinations.*

C. E. TILLEY. *Genesis of Rhombic Pyroxene in Thermal Metamorphism. Mineral Associations and the Phase Rule.*

C. S. GARNETT. *On a Peculiar Chlorite-rock from Ible, Derbyshire. The Dissociation of Dolomite.*

A. BRAMMALL and H. F. HARWOOD. *The Dartmoor Granite: (a) Porphyritic Felspars and Biotite, (b) Andalusite, Sillimanite, Cordierite, and Spinellids.*

J. G. C. LEECH. *Some occurrences of Titanium Minerals on St. Austell Moor.*

## ROYAL SOCIETY OF ARTS.

ARRANGEMENTS FOR MEETINGS DURING  
MARCH, 1923.

Monday, March 5, 8 p.m. (Cantor Lecture).—J. E. SEARS, C.B.E., M.A., M.I.MECH.E., Superintendent of Metrology, National Physical Laboratory, and Deputy Warden of the Standards, *Length Measurement*. (Lecture 1.)

Tuesday, March 6, 4.30 p.m. (Dominions and Colonies Section).—MAJOR E. A. BELCHER, C.B.E., Assistant General Manager, British Empire Exhibition, *The Dominion and Colonial Sections of the British Empire Exhibition, 1924*. The Rt. Hon. L. S. Amery, M.P., will preside.

Wednesday, March 7, 8 p.m. (Ordinary Meeting).—PROF. E. P. STREBBING, M.A., F.L.S., Professor of Forestry, University of Edinburgh, *The Forests of North Russia and their Economic Importance*. The Rt. Hon. Lord Clinton, Forestry Commissioner, will preside.

Monday, March 12, 8 p.m. (Cantor Lecture).—J. E. SEARS, JUN., C.B.E., M.A., M.I.MECH.E., Superintendent of Metrology, National Physical Laboratory, and Deputy Warden of the Standards, *Accurate Length Measurement*. (Lecture 2.)

Wednesday, March 14, 8 p.m. (Ordinary Meeting).—SIR WILLIAM WARRENDER MACKENZIE, K.B.E., K.C., President of the Industrial Court, *Industrial Arbitration*. Lord Askwith, K.C.B., K.C., D.C.L., Vice-President of the Society and Chairman of the Council, will preside.

Friday, March 16, 4.30 p.m. (Dominions and Colonies and Indian Sections).—LT.-COL. SIR LEONARD ROGERS, C.I.E., F.R.S., F.R.C.P., F.R.C.S., Physician and Lecturer, London School of Tropical Medicine, *Recent Advances towards the Solution of the Leprosy Problem*.

Monday, March 19, 8 p.m. (Cantor Lecture).—J. E. SEARS, JUN., C.B.E., M.A., M.I.MECH.E., Superintendent of Metrology, National Physical Laboratory, and Deputy Warden of Standards, *Accurate Length Measurement*. (Lecture 3.)

Wednesday, March 21, 8 p.m. (Ordinary Meeting).—F. W. EDRIE-GREEN, C.B.E., M.D., F.R.C.S., *Some Curious Phenomena of Vision and their Practical Importance*. Prof. E. H. Starling, C.M.G., F.R.S., will preside.

On Monday, March 12, J. E. SEARS, JUN., C.B.E., M.A., M.I.M.E., Assoc.M.-Inst.C.E., Superintendent of Metrology

Dept., National Physical Laboratory, gave his second Cantor Lecture, entitled *Accurate Length Measurement*.

## THE INSTITUTE OF METALS.

At the Annual General Meeting of the Institute of Metals, held in London, on Wednesday, March 7, the following officers were elected to serve for the year 1923-24:

*President*: Leonard Sumner, O.B.E., M.Sc.

*Past-Presidents*: Sir Gerard A. Muntz, Bart., Engineer Vice-Admiral Sir Henry J. Oram, K.C.B., F.R.S., Sir George Heilby, Kt., F.R.S., LL.D., Professor H. C. H. Carpenter, M.A., Ph.D., A.R.S.M., F.R.S., Engineer Vice-Admiral Sir George Goodwin, K.C.B., LL.D.

*Honorary Treasurer*: A. E. Seaton, London.

Sixty new members were elected, bringing the membership total to 1,458. The next election is due to take place on April 19. Particulars can be obtained from the Secretary, Mr. G. Shaw Scott, M.Sc., 36, Victoria Street, London, S.W.1.

## NOTICES OF BOOKS.

*Theophrastus Bombastus von Hohenheim called Paracelsus*, by JOHN MAXSON STILLMAN. Pp. X. + 183. London: The Open Court Publishing Co., 149, Strand, W.C.2. Price 10s.

For almost four centuries the name and fame of Paracelsus have come down to us with something of the legendary haze of fables. Not all that is associated with his name can truly be ascribed to him. Recent investigations have indicated how greatly his teachings and practices revived a spirit of scientific enquiry in medicine and chemistry.

It is interesting to note that, in conformity with the custom of the times, Hohenheim adopted the Latin name Paracelsus, yet he delivered his discourses at Basel and elsewhere in German.

He was a very zealous, original writer, and distinguished himself by being very critical of the time-honoured ideas and methods of his age. The accusation that he was intolerant is probably true, since

he violently opposed all the works and methods of Galen, although these contained much that was true.

It appears that Paracelsus wrote no definitely chemical or alchemical treatises, but in many of his medical and philosophical writings he contributed much to early chemical knowledge. He developed the theory of the three elements—sulphur, mercury, and salt—but his theoretical views were naturally fanciful, and might even be styled unscientific.

However, he made one thing clear, namely, that the transmutation of metals was not the sole aim of alchemy, and that attention could be more profitably directed to the discovery of curative medicaments.

The present biography of Paracelsus is probably the best in existence, dealing as it does in a fair and scientific manner with his stormy and nomadic career, and his influence upon contemporary and later science and medicine. The volume will undoubtedly be widely read by chemists and students interested in the history of their science. J.G.F.D.

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*Discoveries and Inventions of the Twentieth Century*, by EDWARD CRESSY. Second edition. Pp. XXIII. + 453. London: George Routledge & Sons, Ltd. 1922. Price 12s. 6d. net.

The first edition of this excellent book appeared in 1914, and the general scope of the work remains very much the same as previously. As the result of the war we have passed through a period of intense activity in discovery and invention, and therefore considerable alterations have been made to bring all the subjects dealt with previously up to date. In only one instance has no attempt been made to carry out the necessary revision, and in this case *Ships of War and their Weapons*—the information available was not sufficiently reliable to render such revision possible, and so the chapter has been omitted altogether. In its place a new chapter appears, which endeavours to give an elementary account of some of the achievements of modern chemistry, especially in relation to physics and biology, under the title, "The Borderland of Chemistry."

This chapter is divided into sections, and the subjects dealt with are colloids,

the utility of froth, catalysis, fermentation and vitamins. The treatment appears adequate in each case. In the section dealing with colloids we find the following statement: "Many sols are only stable in the presence of an electrolyte." Of course it should read that the absence of electrolytes favours the stability of certain sols. This is an unfortunate error, but readers should easily detect it. Again, when speaking of oleum in the section on catalysis, oleum is given the formula  $H_2S_2O_7$ , which is incorrect. Actually, oleum is simply a solution of sulphur trioxide in sulphuric acid, and has no fixed composition. In industry, certain more or less standard strengths of oleum are met with, such as 20 per cent. and 60 per cent.—this percentage figure simply referring to the content of sulphur trioxide in the oleum.

Generally speaking, the book is well published, and the illustrations are good, but we have noticed a few minor errors, such as "sodium chlorine" for "sodium chloride" (p. 433), and the spelling of radioactivity on page 442. Such errors are perhaps pardonable, and accordingly we have no hesitation in recommending this book to all those who desire to have a non-technical account of the chief scientific and material triumphs which man has achieved and is achieving at the present time.

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#### BOOKS RECEIVED.

*Skinner's Cotton Trade Directory*, by THOMAS SKINNER & Co. Pp. CCLVI. + 1,504. 1923. Messrs. Thomas Skinner & Co., Gresham House, E.C.2. 12s. 6d. net.

*Back to Prosperity: A New Aspect of Practical Life*, by HENRY LOWENFELD and his Daughter, MARGARET LOWENFELD. Pp. 268 + XI. 1923. Effingham Wilson, 16, Copthall Avenue, E.C.2. 5s. net.

*The Mathematical Theory of Relativity*, by A. S. EDDINGTON. Pp. IX. + 247. 1923. The Cambridge University Press, Fetter Lane, E.C.4. 20s. net.

The U.S. Dept. of the Interior has issued the following bulletins:—

*The Inorganic Constituents of Marine Invertebrates*, by FRANK WIGGLESWORTH CLARKE and WALTER COLBURN WHEELER.

*Preliminary Report on Fossil Vertebrates of the San Pedro Valley, Arizona*, by JAMES W. GIDLEY.

*The Shapes of Beach Pebbles*, by CHESTER K. WENTWORTH.

*Forty-third Annual Report of the Director of the United States Geological Survey to the Secretary of the Interior.*

*Gold, Silver, Copper and Lead in South Dakota and Wyoming in 1921*, by C. W. HENDERSON.

*Gold, Silver, Copper, Lead and Zinc in Utah in 1921*, by V. C. HEIKES.

*Manufactured Gas and By-products in 1920*, by R. S. McBRIDE.

*Electric Brass Furnace Practice*, by H. W. GILLETT and E. L. MACK.

*Preparation of Light Aluminium Copper Casting Alloys*, by R. J. ANDERSON.

*Surface Water Supply of the United States, 1918, Part III.—Ohio River Basin.*

*Surface Water Supply of the United States, 1919-1920. Part VII.—Lower Mississippi River Basin.*

*High-Grade Clays of the Eastern United States*, by H. RIES, W. S. BAYLEY, and others.

*Phytographic Provinces and Sections in Western Oklahoma and Adjacent parts of Texas*, by NEVIN M. FENNEMAN.

*General Features of the Magnetite Ores of Western North Carolina and Eastern Tennessee*, by W. S. BAYLEY.

*Peridotite Dikes in Scott County, Arkansas*, by HUGH D. UNKER and CLARENCE S. ROSS.

*Geology of the Ranger Oil Field, Texas*, by FRANK REEVES.

*The Brooks, Steen and Grand Saline Salt Domes, Smith and Van Zandt Counties, Texas*, by SYDNEY POWERS and OLIVER B. HOPKINS.

*Chromite of Kenar Peninsula, Alaska*, by A. C. GILL.

*Geology of the York Tin Deposits, Alaska*, by E. STEIDTMANN and S. H. CATHCART.

*Natural Gas Manual for the Home.*



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 4503—Basset, L. P.—Process for direct reduction of iron, etc., ores. Feb. 16.  
 4140—Berlin, D. W.—Method of reducing metallic oxides. Feb. 12.  
 4064—Dutt, E.—Extraction of radio-active constituents from titaniferous materials. Feb. 12.  
 4065—Dutt, E.—Separation of hafnium from titaniferous materials. Feb. 12.  
 4619—Jques, A.—Manufacture of ammonium sulphate of chrome. Feb. 15.  
 4619—Jaques, A.—Manufacture of ammonium compounds. Feb. 16.  
 4509—Maydegger, O.—Process of manufacturing sulphate of chrome. Feb. 15.  
 4619—West, J. H.—Manufacture of ammonium compounds. Feb. 16.

#### Specifications Published this Week.

- 192426—Reid, J. H.—Reduction of ore and the production of gas.  
 192438—Akt-Ges Fur Anilon-Fabrikation.—Manufacture of new-ortho-oxazo dyestuffs.

#### Abstract Published this Week.

- 191215—Barium Oxide.—Dietrich, W. von, Coswig, Anhalt, Germany.

The manufacture of barium oxide by the action of heat on a mixture of barium carbonate and a reducing agent such as carbon, pitch, tar, or the like, is carried out under reduced pressure in a rotary furnace or a furnace provided with means for agitating the reaction mixture. The furnace is preferably heated internally by electrical means, but heat may be applied instead, or in addition, from the outside. In an example a mixture of 100 kgs. of barium carbonate and 7 kgs. of carbon is heated to 1,000-1,100° C., under a pressure of 65-70 cms. of mercury.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the official price of 1s. each.







phosphorus is pentavalent. When the pressure is reduced the valency is reduced, also, from 5 to 3. The same thing happens in the case of  $\text{NH}_3$  and  $\text{HCl}$ , except that the reaction takes place at (our present) "ordinary temperature and pressure."

The changes in valency with changes of temperature are very significant. Representing an atom by a circle, and showing only the interchanged electrons (by dots), we can represent a molecule of, say,  $\text{NaCl}$ , thus (Fig. VI):—



Fig. VI.

the chlorine drawing an electron from the sodium atom towards it. It may either be included in the outer ring of electrons in the chlorine atom or oscillating between the two atoms. Both the sodium and chlorine atoms become ionic, and within each atom there is a readjustment in the orbits of the electrons to meet the new situation. As temperature rises, the  $\text{NaCl}$  is decomposed, the electronic "link" snapping or ceasing to function. From the practical point of view of formation of compounds, all elements are non-valent towards each other above a certain temperature, as they are below a certain temperature. Even sodium and chlorine which unite with such vigour at ordinary temperatures, will not combine below ; as the temperature falls, polymerisation or association is often increased so that the valency which causes polymerisation is less strong than that required for combination between unlike atoms. We might tabulate the results as follows:—

(1) At very high temperatures, say, the temperature of the sun, Sodium and chlorine are non-valent towards each other.

(2) At ordinary temperature, Sodium and chlorine are approximately monovalent towards each other, uniting to form  $\text{NaCl}$ .

(3) At very low temperatures, Sodium and chlorine are non-valent towards each

other; but molecules of sodium associate with other molecules of sodium and molecules of chlorine with other molecules of chlorine. Sodium must be at least divalent, making no distinction at present between primary and secondary valencies.

These facts have more than a passing interest for us because throughout the whole range of temperature through which the universe has passed, or will pass, say, from  $20,000^\circ \text{C}$ . to the absolute zero, it is only through a relatively small range of temperature that life in any form is possible. On valency depends the formation of compounds—organic compounds for food, organic compounds present in the make-up of a living organism—all of which are destroyed when heated over a small range of temperature. Whatever the genesis of life (as we know it in the material world), unless it gets a foothold during this vital range of temperature, life, either on the earth, or Mars, or other celestial bodies, is impossible.

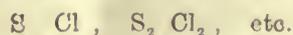
Many chemical compounds might be mentioned to show that the valency of one element for another element frequently varies even within the valency-limits just referred to; e.g., the chlorides of sulphur.

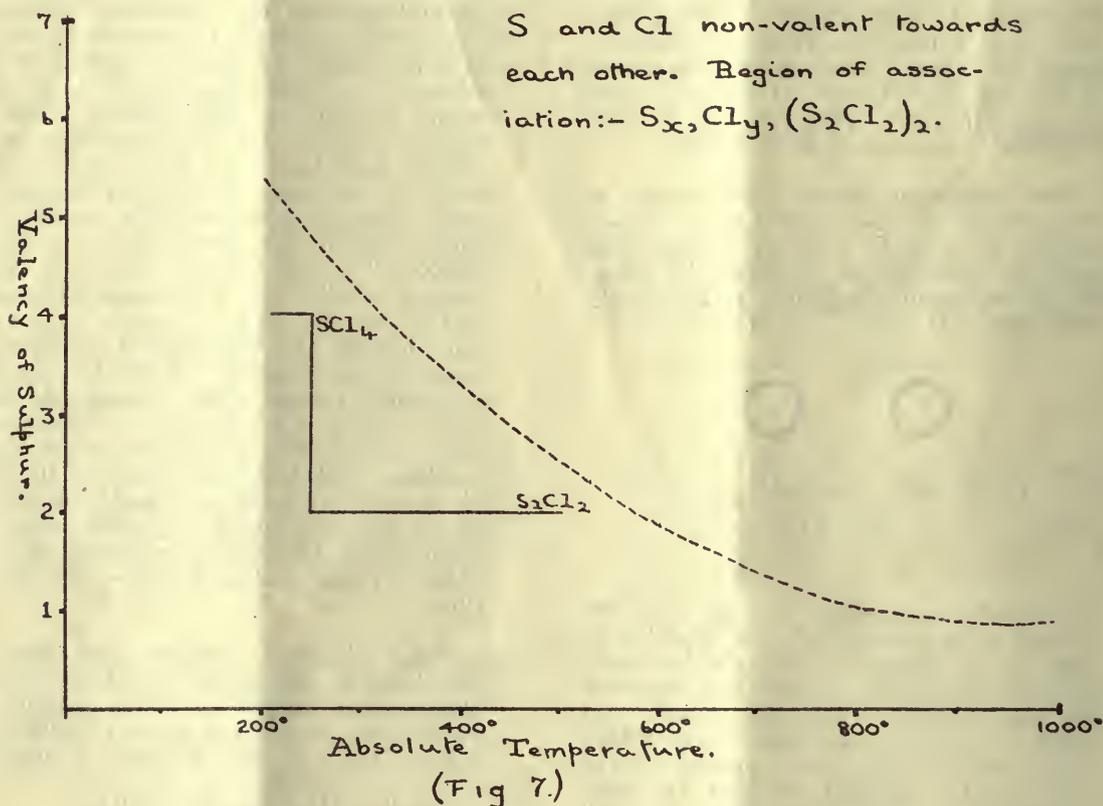
#### Sulphur Monochloride ( $\text{S}_2\text{Cl}_2$ ).

B.p.	$138^\circ \text{C}$ .	( $411^\circ \text{A}$ )
M.P.	$-80^\circ \text{C}$ .	( $193^\circ \text{A}$ )

This liquid saturated at  $251^\circ \text{A}$  with chlorine is transformed into  $\text{SCl}_2$ , M.P.  $242^\circ \text{A}$ . On removing it from the freezing mixture the valency is reduced and  $\text{S}_2\text{Cl}_2$  and  $\text{Cl}_2$  are again formed. These changes are shown in the diagram (Fig. VII.)

The valency between sulphur and chlorine is shown in steps. At  $251^\circ \text{A}$ . thirty-two parts by weight of sulphur can "hold" 142 parts of chlorine; at a higher temperature only 35.5 parts of chlorine. There may be an intermediate point where 32 parts of sulphur are satisfied by 60 or 80 parts of chlorine if there existed a standard substance with which they could be compared; only as union between sulphur and chlorine takes place in atoms and not in fractions of an atom, the compounds of sulphur and chlorine must be





The dotted line shows the possible value of the valency of sulphur for chlorine and accounts for the "residual" valency which is used to account for the formation of polymers, complex atoms, etc.

Water might be quoted as another example. At high temperatures it is dissociated into hydrogen and oxygen (when

they become non-valent towards each other); between 0° and 100° C. not only is  $H_2O$  present, but varying amounts of  $(H_2O)_2$ , and  $(H_2O)_3$ . The formation of the latter postulate a higher valency for either hydrogen or oxygen, or both.

(To be Continued.)

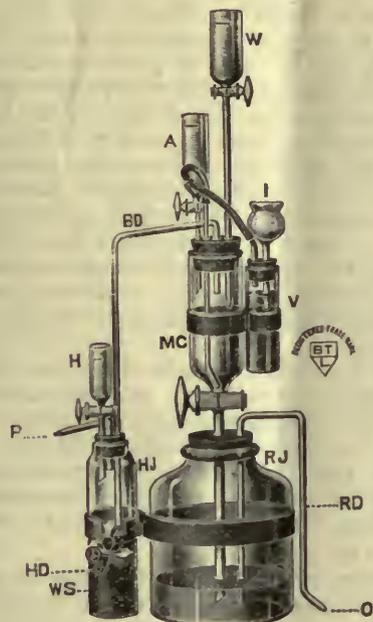
#### ON THE USE OF POTASSIUM OR SODIUM BROMIDE AS A SOURCE OF BROMINE FOR UREA ESTIMATIONS.

By C. H. COLLINGS.

In urine analysis the estimation of urea is usually carried out by means of the interaction of sodium hypobromite and the urine to be analysed. Sodium hypobromite, as such, cannot be kept in stock, and has therefore to be made shortly before use, by the addition of bromine to sodium hydrate solution. Bromine in its native form needs extreme care in handling if unpleasant consequences are to be avoided, it

is expensive, and its carriage is costly and subject to delay, and in some cases (such as India) is prohibited altogether. It follows, therefore, that a method of obtaining and handling bromine that is at once safe in even unskilled hands, is economical, and is unaffected by such prohibition, may be regarded as of some practical utility. I am not disregarding the usual laboratory methods for the evolution of bromine from its compounds, but the advantage in practice of the method here described is evident.

The apparatus previously described and figured respectively in *The Chemical News* (this vol., pp. 55 and 95, Jan. 26 and Feb. 9) is used.



It is connected up with an aspirator or pump, and air is drawn steadily through it during the whole operation. The rôle of the air is rather important. It not only exercises an obviously useful mechanical function, but directly contributes to the separation and removal of the Br from the mixed fluids in which it first finds itself on disengagement from its chemical tie with potassium or sodium, the air passing through the mixed fluids from bottom to top.

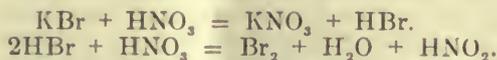
The method is as follows: Make a stock solution of potassium or sodium bromide, in the proportions of 10 grams of potassium bromide to 25 cc. of distilled water (or NaBr 8 gr. to 25 cc. water). Twenty-five cc. of sodium hydrate solution of the usual hypobromite formula are introduced into HJ via the cup H, and its tap turned off. Fifteen cc. of nitric are placed in A, and at once run into MC and the tap turned off. Twenty cc. of KBr or NaBr solution are placed in W.\* The aspirator is now started, and the tap of W turned on, about 10 drops only admitted, and the tap closed again. The aspirator must be kept going during this and the whole of the subsequent operations. (Should a break be necessary for later readjustment, the tap W must be turned off meantime.)

A curious feature now arises. The mixed bromide solution and the acid de-

velop a strong reddish colour, which is transparent. This persists for about three minutes; then, with remarkable suddenness, an opacity develops in the mixture and becomes absolute. This, of course, is the sign of bromine evolution; the air current picks it up, and the sodium hydrate solution in HJ begins to show a yellow tinge (hypobromite formation); and the tap of W should at once be turned on to give 60 drops a minute or faster, provided that no bromine is observed to condense on the walls of MC, or sediment just over its discharge tap at the bottom. Brown fumes of nitrous acid may also be observed in the air in MC; these are also carried over and neutralised by the sodium hydrate, of which the formula provides an ample margin for spare alkalinity.

The air should be kept passing after all the bromide solution is in and until the mixed acid and bromide loses its opacity and regains its former deep orange-red transparency. The hypobromite will now be ready for use and may be drawn off by the delivery tap HD.

The obvious equations for the reaction are:—



Should any crystals ( $\text{KNO}_3$ ) be precipitated at the bottom of MC, they are readily soluble in a little water, subsequently.

As regards cost, that of a 2.2 cc. tube of bromine is about 7d.; of potassium bromide to produce an equivalent amount, somewhere between a halfpenny and a penny. To this must be added the value of 15 cc. of nitric acid.

The details of the apparatus not already described are as follows: I is the air inlet to valve V—this is nearly filled as shown with sodium hydrate solution to trap any back pressure of bromine. BD is the tube that delivers the free bromine into HJ containing the waiting sodium hydrate solution, which (HJ) is supported on W. The aspirator or pump is connected up at P. The large jar, RJ, takes the residual fluid from the operation at its conclusion, via the tap below MC, and is periodically syphoned empty via the tube RD, discharging at O.

\* The full amount to correspond to 2.2 cc. Br should be about 27.5 cc., but this really represents an excess over usual needs.

### SCIENTIFIC INVESTIGATIONS ON METAL POLISHING AND GRINDING.

A lecture was given recently at the Chamber of Commerce, Birmingham, by Mr. Dartrey Lewis, M.Met., describing an investigation on the materials used in metal polishing, which he has undertaken for the British Non-Ferrous Metals Research Association.

This work has been carried out at the Sheffield University, under the supervision of Professor Desch, F.R.S., Dean of the Faculty of Metallurgy.

In introducing the lecturer, Dr. R. S. Hutton, Director of the British Non-Ferrous Metals Research Association, explained that the lecture would describe the first fruits of one of a series of researches, undertaken by this Association, on problems of direct practical importance to the Metal Industries. The polishing process played a very important part in the production of every variety of metal articles, and in general, accounted for a high fraction of the cost of production. In Sheffield and Birmingham, buffers and metal polishers totalled many thousands, their work was laborious and frequently highly skilled, but little had been done to explore possibilities of improvement. A previous investigation with which he had been connected had been devoted to the more human side of the process, and in connection with this, he had visited a French factory, where an output in spoon and fork buffing of two to three times that usual in this country had been achieved. Such cases should serve as an incentive to industrial research.

Mr. Dartrey Lewis explained that he had devoted his attention to investigating the fundamental properties of the materials used in metal polishing, sand, pumice, emery, etc. Methods had been devised for measuring the abrading or cutting power of these materials on brass and other metals in the loose powdered form in which they are generally used. The relative durability of the materials, or the useful life of their grains before they broke down into too fine a state of division to effect any more useful grinding, had also been measured.

Information of this nature appeared to be completely lacking, although, of course, the experts in the trade possessed a vast amount of accumulated experience. The necessity for quantitative comparative measurements was all the greater, because in recent years new abrasive materials,

such as artificial corundum and carborundum had been discovered of much better grinding power, and of greater durability. This experimental work supplied certain basic information, but it was for the industry to consider how far and in what directions one material was superior to another for any given works process. It was, however, suggested that advantage might be taken of some of the superior materials to remove the rougher and thicker layers of metal, whilst still using sand and pumice for smoothing off preparatory to the real polishing.

Mr. Lewis also briefly described his experiments in comparing chromic oxide and rouge for polishing steel and silver.

The British Non-Ferrous Metals Research Association is extending the investigation to "glazing" and other abrasive processes, in which the abrasives are fixed to wheels by glue.

In view of the widespread use of polishing processes it is hoped that this work will attract to the Association the support of many firms in branches of the metal industry hitherto unrepresented in its membership.

### NOTE ON p-NITROBENZYL-PYRIDINIUM SALTS.

By H. H. GRAINGER, B.Sc., A.I.C.

In the course of some experiments on the tinctorial properties of azo-dyes containing the pyridinium group it became necessary to prepare dyes from aminobenzylpyridinium salts. Lellmann and Pekrun (Annalen, 1890, CCLIX., 52) found that p-nitrobenzylchloride reacts easily with pyridine to give a quaternary salt, although they did not analyse the product, which they describe as forming yellow prisms which sinter at 90° and melt at 103°. They, however, were obviously dealing with a very impure product, and it has now been found that if the chloride is purified by recrystallisation from a mixture of alcohol and ether, it forms a snow-white crystalline powder which melts and decomposes sharply at 208°. (Found: Cl = 13.9.  $C_{12}H_{11}O_2N_2Cl$  requires Cl = 14.2 per cent.)

The corresponding bromide is readily obtained by the action of pyridine on p-nitrobenzylbromide, and is best purified by recrystallisation from alcohol and ether. It melts at 222°. (Found: C = 48.6, Br

= 27.0.  $C_{12}H_{11}O_2N_2$  Br requires C = 48.8, Br = 27.1 per cent.)

The addition of picric acid to a solution of the chloride or the bromide gives an immediate precipitate of the very sparingly soluble *picrate* which can be recrystallised from boiling water and then forms beautiful glistening yellow needles which melt at  $172^\circ$ . (Found: N = 15.8,  $C_{18}H_{13}O_9N_5$  requires N = 15.8 per cent.)

By reducing aqueous solutions of the chloride by means of tin and hydrochloric acid, solutions of the aminobenzylpyridinium salt can be obtained. These were sulphuretted hydrogen, and the result freed from tin in the usual way by ing solution then diazotised and coupled with  $\beta$ -naphthol, dimethylaniline and R-salt. By this means very soluble, red, basic dyes were obtained, but these proved to be far too unstable to be of any technical value.

Sir John Cass Technical Institute,  
Jewry St., Aldgate, London, E.C.3.

## THE SPEED OF CHEMICAL REACTION THROUGH A SOLID.

By C. D. NIVEN.

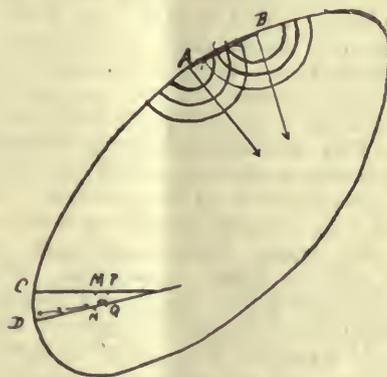
Much work has been done on Chemical Reaction in Solution, but the reactions of a solid with a solution seem to have fallen into the background. There are, however, many reactions of this kind.

The object now in view is to determine the theoretical time for a reaction to go through a solid of definite shape and size, the solvent being semipermeable to the solid.

Two cases arise. First, when the solute, *i.e.*, the reactive part of the solution, renders the solid more impermeable to the solvent, and secondly, less impermeable; but as it is the permeability after reaction is complete that determines the speed of reaction, the former of these cases is the important one. It is very important in such a case to know when the reaction has reached the centre of the body. Obviously the shape of the body would determine to some extent the time required to reach the most distant point from the surface, and a small increase in thickness in certain bodies might cause enormous increase in the time required to complete the reaction,

if the material of which the body was composed became very impermeable after the reaction.

— In the case of a solid body in a solution which reacts with the solid body semipermeable to the body before and after reaction, it is seen that each point on the surface of the body is a starting point for reaction.



Taking a point A on the surface, the chemical can be supposed to find its way into the solid like a ray of light shining through a pin-hole on a surface and spreading in concentric spherical shells. If a point B be taken near the point A, similar currents start in all directions, but the currents from B resolved along BA, and which act in that direction, are counter-balanced by the currents emanating from A resolved along AB in direction AB. Therefore the main reaction travels perpendicular to the line AB; that is to say the reaction travels into the body in the direction of the normal to the curve or surface.

As the solid is semipermeable to the solvent in which the chemical is dissolved, it is reasonable to imagine that the solvent really acts as a carrier. For simplicity it is assumed that the body is cylindrical in shape. This permits dealing with a curve instead of a surface, as the reaction would clearly travel at the same speed through any cross-section.

Let C D N be a section, C and D two points near on the surface, and CM and DN normals respectively at C and D; and let the reaction reach M and N at the same time, say  $t$ , and let it reach P and Q in time  $\delta t$ .

Let  $CM = x$  and  $MP = \delta x$ .

Then as C and D are near  $CN = x$  and  $NQ = \delta x$ , the area acted on in time  $\delta t$  is  $MNQP = MN\delta x$ .

The amount of chemical required to act on this area is proportional to the area.

The distance the chemical has to come is  $CM = x$ .

But as CD is greater than MN in a convex curve, the chemical could travel much more quickly near CD than near MN, as the molecules would pack up together as they travelled in. The solid material only being semipermeable to the solvent will have a certain restraining effect to the reaction. This will depend on the nature of the substances reacting, and in most cases on the concentration of the solution.

In order to visualise what has been said above, the reader may imagine an area covered with causeway or concrete, which has to be covered to a depth of a foot with sand, beginning from the outside—as many vehicles of transport being allowed to work. The farther from the edge, the harder the work becomes, as in the first place the distance is greater, in the second place fewer vehicles can work as there is no room near the centre, and in the third place the sand renders the ground to be covered more difficult. From this analogy, it is easy to see that the number of molecules that could pass in at a time, *i.e.*, number of vehicles, is proportional to the width of the passage or road, and in a wedge-shaped passage the number would be proportional to the area of wedge divided by the length of distance.

Turning again to Fig. I., the time to complete the chemical reaction on the small area MNQP is (1) proportional to distance chemical has to come, (2) inversely proportional to average width of passage, and (3) proportional to amount of chemical required,

$$\begin{aligned} \text{i.e., Time} &= K x \frac{x}{AMNB} \times MN\delta x \\ &= K \frac{x^2 MN \delta x}{AMNB} \end{aligned}$$

∴ Total time to react from outside to a distance  $x_1$  is

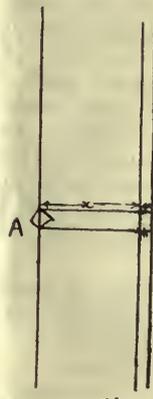
$$\int_0^{x_1} \frac{K x^2 MN \delta x}{AMNB}$$

In the case of a body of any shape instead of the piece of curve MN, there is a small curved area, and instead of the

wedged area AMNB is a frustum of a cone.

Three important forms of solid deserve special investigation, *viz.*, the plane surfaced plate, the cylinder of circular section, and the sphere.

In the first case when the surface is plane the normals are all parallel and the line of the reaction always advances parallel to the surface.



Considering a small area, A, on the surface, the time to react at a distance  $x$  on same size of area is

$$K x \frac{x}{Ax} \times A dx$$

$$\begin{aligned} \text{Total time} &= \int_0^{x_1} K x dx = \frac{Kx^2}{2} \\ &= K x_1^2 \end{aligned}$$

In the case of a cylinder of circular section, the value of MN in terms of  $x$  and the radius of the circle is required, and also a value for the area AMNB in the same terms. If "a" be the radius of circle and  $\alpha$  = angle AOB where O is the centre, then  $MN = a(a-x)$  . . . (1)

$$\begin{aligned} \text{Area AMNB} &= \text{AOB} - \text{MON} \\ &= \frac{1}{2} a (a^2 - a^2 - x^2) \\ &= \frac{1}{2} a (2ax - x^2) \end{aligned} \quad \text{. . . (2)}$$

Hence, total time to depth  $x$ ,

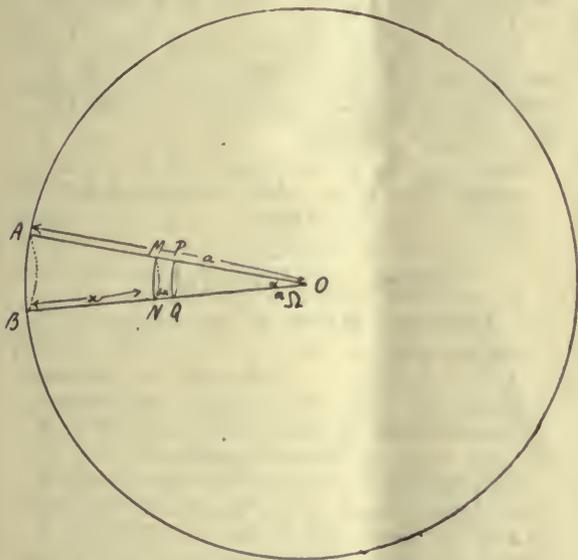
$$\int_0^{x_1} \frac{K x^2 \cdot a \cdot a - x dx}{\frac{1}{2} a \cdot x (2a - x)}$$



$$\int_0^{x_1} \frac{K 2x(a-x) dx}{2a-x}$$

Substituting  $z$  for  $2a-x$  and integrating,  
 Total time =  $2K \left[ \frac{3aZ - Z^2}{2a - x_1} - 4a \log Z \right]_{2a - x_1}^{2a}$   
 To complete the reaction to the heart put  $x_1 = a$ . The total time then becomes  $Kx \cdot 2276a^2$ .

In the third case, viz., a sphere of radius "a," it is required to find a value of the small area MN and the volume of the frustum ABNM.



Let the area AB subtend a solid angle  $\Omega$  at the centre O. Then the area MN is

$$\Omega : a - x^2 \quad \text{---} \quad (1)$$

$$\frac{1}{3} \Omega [a^3 - a - x^3] \quad \text{---} \quad (2)$$

Substituting in the general formula found above, the total time to a depth  $x_1$  is

$$\int_0^{x_1} \frac{K : x^2 : \Omega : a - x^2 dx}{\frac{1}{3} \Omega [a^3 - a - x^3]} = 3K \int_0^{x_1} \frac{a - x^2}{x^2 - 3ax + 3a^2} x dx$$

On integration, the total time is

$$= \frac{3K}{2} \int_0^{x_1} \frac{x^2}{x^2 - 3ax + 3a^2} dx + 3Ka^2 \log \dots$$

$$\int_0^{x_1} \frac{x^2 - 3ax + 3a^2}{x^2 - 3ax + 3a^2} dx$$

$$= 3\sqrt{3}K a^2 \tan^{-1} \left[ \frac{x - \frac{3}{2}a}{\frac{\sqrt{3}a}{2}} \right]$$

$$= 3K \frac{x_1^2}{2} + 3K a x_1 + 3K \frac{a^2 \log}{2} \frac{x_1^2 - 3ax_1 + 3a^2}{3a^2}$$

$$- 3\sqrt{3} K a^2 \left[ +an^{-1}(-\frac{1}{3}) - +an^{-1}(-\sqrt{3}) \right].$$

When the reaction reaches the heart of the sphere  $x_1 = a$  and the total time becomes

$$K a^2 \times 0.1271.$$

The times then for a plane plate of thickness  $2a$ , a circular cylinder of radius  $a$ , and a sphere of radius  $a$ , are in the proportion of 0.5 : 0.2276 : 0.1271, no matter what the reacting chemical is, or its strength, provided, of course, it does react according to the original assumption.

To demonstrate, the following is a practical example. In a bath of formaldehyde various pieces of casein plates were steeped from 3 millimetres upwards, and various pieces of cylinders, all circular in section and solid.

These were watched and the times when the reaction was completed were noted. Each piece, when ready, was dried and measured in a micrometre. The values for plates were found to be very near the curve  $y = 888x^2$ , where  $y = \text{time}$  and  $x = \text{thickness}$ .

A curve may then be plotted and the points found by experiment marked

The following is a table showing the times got by experiment and the times agreeing with the theoretical curve for plates  $y = 0.888x^2$  :—

Thickness in mm.	3.3	4.6	5.8	7.5	13
Expt., days .....	9	19	32	50	140
Theor., days. ....	9.6	18.8	29.9	49.9	150

For the rods the curve is fixed assuming the solution is the same as for the plates, viz.,  $y = 0.404x^2$ , and the following are the experimental values and the theoretical values of the times for certain thicknesses of rods :—

Diameter in mm.	5	7.8	10	12.7	17.9
Expt., days .....	11	25	38	61	133
Theor., days .....	10.1	24.6	40.4	65.2	130

The values are sufficiently near to justify the theory proposed above as the difficulty in getting the exact end point in a very slow reaction is of course great.

Owing to the expense of getting moulds made for spheres, it has been impossible to get a series of readings, but one sphere was taken and compared under similar conditions with a 5 mm. plate or sheet—more rapid conditions than those under which original pieces were tested.

The 5 mm. plate took 14 days and the sphere 13 mm. in diameter took 25 days. Calculating what time this sphere would have taken if the 5 mm. sheet took 14 days, we get

$$\frac{0.1275}{0.5} \times \frac{169}{25} \times 14 = 24.05 \text{ days.}$$

This supports the theory.

#### GENERAL NOTES.

##### ACETONE FOR THE UNITED STATES.

Mr. G. Campbell, H.M. Consul-General in San Francisco, reports that a local firm of manufacturers of compressed acetylene gas are desirous of getting into touch with United Kingdom manufacturers of acetone for the purpose of purchasing supplies for use in their business. The acetone must comply with the British War Office specifications. The enquirers are understood to enjoy a very good standing and reputation, and they stipulate that quotations should state price per pound F.A.S. British shipping port on quantities of approximately 30,000 pounds. The price must be in competition with that of 21 cents per pound in the United States.

An import duty of 25 per cent. *ad valorem* is levied on acetone imported into the United States.

The name and address of the firm in question may be obtained by manufacturers on application to the Department of Overseas Trade (Room 52).

Sir Eric Geddes, President of the Federation of British Industries, delivered an important speech on the Trade Future, at Birmingham, on Tuesday, March 13, on the occasion of the Annual General Meeting of the West Midland Branch of the F.B.I.

The Department of Overseas Trade has just issued a small explanatory handbook, indicating the aims and objects of the Department, and the directions in which it is intended to assist and develop commerce.

##### CRESYLIC ACID FOR THE UNITED STATES.

Mr. D. H. M. Sinclair, H.M. Consul-General at Philadelphia, reports that a local firm of wholesale oil dealers desire to receive from U.K. manufacturers quotations for cresylic acid 97 to 99 per cent. pure, straw colour, and 95 to 97 per cent. pure, dark, as well as lower grades.

The name of the firm may be obtained by interested firms upon application to the Department of Overseas Trade.

The British Vice-Consul at Constantza (Mr. Tottenham Smith) reports that a local authority desires to be put in touch with United Kingdom suppliers of medico-surgical instruments necessary for a complete polyclinic, including X-ray equipment, and to receive copies of catalogues, in French if possible.

Further particulars, together with the name and address of the enquirer, can be obtained by firms on application to the Department of Overseas Trade.

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL SOCIETY.

THURSDAY, MARCH 15, AT 4.30 P.M.

Papers read:—

J. A. CARROLL. *Note on the Series-Spectra of the Aluminium Sub-Group.* Communicated by Prof. A. Fowler, F.R.S. (Paper read by communicator.)

In contradistinction to the alkali metals, the highest terms in the known series-spectra of the elements of the aluminium sub-group are the common limits of the sharp and diffuse series, and not the limits of the principal series.

Measurements of the ionisation and resonance potentials for thallium, however, have suggested that there might be a yet undiscovered principal series in the far ultra-violet, the limit of which would be the greatest term and would correspond with the normal state of the thallium atom. In the present paper it is pointed out that against this is the absence of positive evidence of such a series, and the easily reversible nature of the lines of the subordinate series in the arc spectra.

It seemed that valuable evidence as to the normal state of the atoms might be afforded by an investigation of the absorp-

tion spectrum of the cool vapour of one of the elements in question. Thallium was chosen as an easily obtainable and representative member of the group, which is not too difficult to deal with experimentally. It was found that the lines obtained in absorption were members of the subordinate series, thus confirming the original series arrangement. The results are in accordance with the latest developments of Bohr's theory, according to which two of the outermost electrons in the thallium atom are in  $6_1$  orbits and one is in a 6 orbit.

W. E. CURTIS, D.Sc. *The Structure of the Band Spectrum of Helium.—II.* Communicated by Prof. O. W. Richardson, F.R.S.

Seven of the doublet bands previously examined by Fowler have been studied in detail, with the following results:—

1. Tables of wave-lengths, etc., and least-square empirical formulæ were given for the constituent series of each band.

2. The structure of the bands was considered. In the main this is in agreement with the requirements of the quantum theory, but some important discrepancies were noted and discussed in connection with Kratzer's half-quantum hypothesis.

3. Values for the moments of inertia of the molecules concerned were derived by a graphic method and used to verify certain theoretical conclusions.

4. Several perturbations were recorded (the first examples in this spectrum), and their significance is discussed.

5. A new combination law was tested and found to be obeyed.

6. Some peculiarities noted by Fowler were verified and explained.

G. C. STEWARD. *Aberration Diffraction Effects.* Communicated by Prof. A. S. Eddington, F.R.S.

Diffraction theory would indicate that the image of a luminous point, given by a symmetrical optical system, should be a system of luminous rings, and this was investigated by Airy in 1834; geometrical theory, on the other hand, leads to a consideration of several types and orders of aberration—the more common ones being better known as the "Five Aberrations of Von Seidel." They are: Spherical Aberration, Coma, Astigmatism, Curvature of the Field, and Distortion. These are well known and have been investigated by a number of writers. In the present paper a consideration is undertaken of the modifi-

cation of the "ideal" diffraction pattern produced by these geometrical aberrations.

The method adopted depends upon the Eikonal Function of Bruns, and a summary of the properties of this function was given, therefore, in Part I. of the paper. Part II. dealt with the Aberration Diffraction effects.

Throughout Parts I. and II. it is assumed that the stops of the optical system are circular, with centres upon the axis of symmetry; and this is generally the case. Occasionally, however, other stops are used, and in Part II. of the paper is undertaken a consideration of the diffraction effects of such in the presence of the various geometrical aberrations. The precise forms of aperture considered are the following:—

1. The usual circular aperture, but with the central portion stopped out.

2. One (or two parallel) narrow rectangular aperture.

3. A semi-circular aperture.

Papers read in title only:—

LORD RAYLEIGH, F.R.S. *Further Observations on the Spectrum of the Night Sky.*

This paper is a continuation of the author's previous studies on the spectrum of the night sky.

Specially designed spectrographs having a working aperture of  $f/9$  are described. The northern and southern horizons have been photographed simultaneously on the same plate, and the aurora line recorded almost down to the horizontal direction in each. It is found, however, that there is no marked difference of intensity between them.

The negative nitrogen bands appear fairly often in photographs of the night-sky spectrum exposed for several nights running in the North of England. Similar spectra taken in the South of England do not show them. As previously shown they are always strong in the Northern Lights in Shetland.

The spectrum of the night sky shows two bright lines or bands in the blue and violet, the approximate positions, as nearly as they could be determined on the *very* small scale spectra, were 4200 and 4435. The origin of these is not known. In addition, there is the aurora line 5578, also of unknown origin, and the dark Fraunhofer lines H and K. These various lines, bright and dark, are shown on a photograph sent

to the author by Dr. E. C. Slipher, which was taken about the same time.

LORD RAYLEIGH, F.R.S. *Studies of Iridescent Colour, and the Structure producing it. IV.—Iridescent Beetles.*

It is shown that some of the iridescent beetles which have striking metallic colours show band systems in the spectrum of the reflected light. Two such spectra are reproduced.

The first, from *Pelidnota sumptuosq.*, shows a central maximum bordered on either side by subordinate maxima in exactly the way that reflection from a quite uniformly spaced assemblage of thin plates would require. The number of planes calculated to be required in this case is no less than 34. A Lippmann film shows a similar spectrum.

The second spectrum is from one of the golden beetles, *Callodes parvulus*. The bands are accounted for on the supposition of two assemblages, each consisting of several reflecting planes, the distance between the assemblages being about  $8\mu$ . This would result in a series of equally spaced bands over a limited range of the spectrum as observed.

The possibility of either of these spectra being produced on the alternative theory of surface reflection is discussed, and is found to require a number of special suppositions which seem very difficult of acceptance.

PROF. J. W. NICHOLSON, F.R.S. *Oblate Spheroidal Harmonics and their Applications.*

PROF. J. W. NICHOLSON, F.R.S., and PROF. F. J. CHESHIRE. *On the Theory and Testing of Right-angled Prisms.*

PROF. J. C. MCLENNAN, F.R.S., and D. S. AINSLIE. *On the Fluorescence and Channelled Absorption Spectra of Cæsium and other Alkali Elements.*

Cæsium has been shown to exhibit a fluorescence and a channelled absorption spectrum in the neighbourhood of  $\lambda = 2000$  when the vapour of the element is traversed by white light. In the absorption spectrum the bands were found to be separated by intervals that were simple multiples of 24 Å. Like sodium, potassium has been shown to exhibit channellings in its absorption spectrum in the neighbourhood of the second member of its doublet series. The fluorescence spectrum of rubidium has been photographed, and the wavelength of its bands measured. Indications have been obtained of channelling in

the absorption spectrum of lithium in the near ultra-violet region.

W. STILES, Sc.D. *The Indicator Method for the Determination of Coefficients of Diffusion in Gels, with special reference to the Diffusion of Chlorides.* Communicated by W. B. Hardy, Sec. R.S.

1. An indicator method is described by which the coefficients of diffusion of chlorides, sulphates and other substances can be simply determined.

2. The coefficients of diffusion of a number of chlorides in 0.5 per cent. agar-agar gels are recorded.

3. The effect of temperature on the coefficient of diffusion of these chlorides has been investigated. The coefficient increases at a greater rate per degree rise in temperature the higher the temperature; the relation between coefficient of diffusion and temperature in gels is thus not a linear one as is usually assumed to be the case for free diffusion in water.

4. The coefficient of diffusion decreases with increasing concentration of gel. Empirical expressions are given to record the relation between coefficient of diffusion and concentration of gel.

5. The coefficient of diffusion increases with decreasing concentration of the diffusing salt. An empirical expression is given to express approximately the relation between coefficient of diffusion and concentration of diffusing salt in the case of sodium chloride.

H. T. FLINT. *A Generalised Vector Analysis of Four Dimensions.* Communicated by Prof. O. W. Richardson, F.R.S.

The paper gives an account of an invariant Vector Calculus in a notation which is the natural generalisation of that of Gibbs. Contravariant and covariant vectors are related by means of an operator—the extended idem-factor, and tensors are introduced as dyadics and polyadics. The expressions familiar in the Tensor Calculus of Riemann and Christoffel appear very simply in the analysis. Separated points are connected by the geodetics and a simple definition of parallelism at two points leads at once to the Weyl parallel displacement relations.

ROYAL INSTITUTION OF GREAT BRITAIN.

The Friday evening discourse on Friday, March 23 (at 9 o'clock) will be delivered by SIR ERNEST RUTHERFORD, LL.D., D.Sc.,

F.R.S., M.R.I., Prof. of Natural Philosophy; Cavendish Prof. of Experimental Physics, Univ. of Cambridge. The subject is *Life History of an Alpha Particle from Radium*.

Saturday, March 24. — SIR ERNEST RUTHERFORD, LL.D., D.Sc., F.R.S., M.R.I., Prof. of Natural Philosophy, on *Atomic Projectiles and their Properties*. (Lecture VI.)

#### ROYAL AGRICULTURAL SOCIETY.

PROCEEDINGS AT MONTHLY COUNCIL, HELD AT 16, BEDFORD SQUARE, W.C.1, ON

WEDNESDAY, MARCH 7.

Lieut.-Col. E. W. Stanforth (President) in the Chair.

Among the reports of the various Standing Committees presented and adopted was the following:—

##### *Chemical Report.*

Lord Bledisloe, in the absence of Mr. Luddington, reported that the Consulting Chemist had presented to the Committee a list of the samples analysed by him for members during the past month.

The Chairman had reported that he, together with Mr. J. W. Pearson, had had an interview with the Minister of Agriculture on the question of the new Bill to amend the existing Fertilisers and Feeding Stuffs Act. Sir Robert Sanders had promised to write his decision in the course of a few days. As this reply had not yet been received, it was decided that a further meeting should not be called until the promised reply from the Ministry was in the hands of the Chairman. Should, however, a considerable time elapse, the Chairman would call another meeting of the representatives.

Dr. Voelcker had submitted various matters arising out of his correspondence, which dealt chiefly with castor oil bean in feeding cakes, basic slag which was insufficiently ground, fish meal with excessive oil, and the cost of burning chalk for lime.

The Committee received with regret the report of the death of Mr. F. J. Lloyd, formerly senior assistant in the Society's laboratory.

Lord Bledisloe, in moving the adoption of this report, referred to the recent death of Mr. Lloyd, who at one time had been an assistant in the Society's laboratory. Mr. Lloyd had done valuable work during his lifetime as an agricultural chemist.

#### THE GEOLOGICAL SOCIETY.

##### ANNUAL GENERAL MEETING.

February 16.—Prof. A. C. Seward, Sc.D., F.R.S., President, in the Chair.

The Reports of the Council and the Library Committee were read.

The completion of Vol. LXXVIII. of the Quarterly Journal was announced, as also the publication of the Lists of Geological Literature for 1914 and 1922.

The President presented the Wollaston Medal to William Whitaker, F.R.S.

The Murchison Medal was presented to Prof. John Joly, F.R.S., the Lyell Medal to M. Gustave F. Dollfus, the For.Memb.-G.S.

The Bigsby Medal was awarded to Mr. Edward Battersby Bailey, M.C. Mr. G. W. Lamplugh, F.R.S., acknowledged it for the recipient.

The ballot for the Council and Officers was taken, and the following were declared duly elected for the ensuing year:—*Council*: Charles William Andrews, B.A., D.Sc., F.R.S.; Frederick Noel Ashcroft, M.A., F.C.S.; Prof. Percy George Hamnall Boswell, O.B.E., D.Sc.; Prof. William S. Boulton, D.Sc., Assoc.R.C.Sc.; James Archibald Douglas, M.A., B.Sc.; Gertrude Lilian Elles, M.B.E., D.Sc.; John William Evans, C.B.E., D.Sc., LL.B., F.R.S.; John Smith Flett, O.B.E., M.A., LL.D., D.Sc., M.B., F.R.S.; Sir Archibald Geikie, O.M., K.C.B., D.C.L., LL.D., Sc.D., F.R.S.; Frederick Henry Hatch, O.B.E., Ph.D.; Robert Stansfield Herries, M.A.; Prof. Owen Thomas Jones, M.A., D.Sc.; William Bernard Robinson King, O.B.E., M.A.; William Dickson Lang, M.A., Sc.D.; Richard Dixon Oldham, F.R.S.; Prof. Sidney Hugh Reynolds, M.A., Sc.D.; Prof. Albert Charles Seward, Sc.D., F.R.S., F.L.S.; Walter Campbell Smith, M.C., M.A.; Sir Aubrey Strahan, K.B.E., Sc.D., LL.D., F.R.S.; Sir Jethro J. Harris Teall, M.A., D.Sc., LL.D., F.R.S.; Herbert Henry Thomas, M.A., Sc.D.; Prof. William Whitehead Watts, LL.D., Sc.D., M.Sc., F.R.S.; and Henry Woods, M.A., F.R.S.

*Officers*: President, Prof. Albert Charles Seward, Sc.D., F.R.S., F.L.S.; Vice-Presidents, John William Evans, C.B.E., D.Sc., LL.B., F.R.S.; Richard Dixon Oldham, F.R.S.; Herbert Henry Thomas, M.A., Sc.D.; and Prof. William Whitehead Watts, LL.D., Sc.D., M.Sc., F.R.S. Secretaries, Walter Campbell Smith, M.C., M.A., and James Archibald Douglas,

M.A., B.Sc.; Foreign Secretary, Sir Archibald Geikie, O.M., K.C.B., D.C.L., LL.D., Sc.D., F.R.S.; and Treasurer, Robert Stansfield Herries, M.A.

The thanks of the Fellows were unanimously voted to Prof. E. J. Garwood and Dr. G. T. Prior, retiring from the office of Vice-President, and also from the Council; and to the other retiring members of Council: Dr. F. A. Bather, Mr. T. C. Cantrill, and Mr. J. F. N. Green.

FEBRUARY 28, 1923.

Prof. A. C. Seward, Sc.D., F.R.S., President, and, afterwards, Prof. W. W. Watts, Sc.D., F.R.S., Vice-President, in the Chair.

The list of donations to the Library was read.

The following communications were read:—

*The Late Glacial Stage of the Lea Valley (Third Report)*, by SAMUEL HAZZLEDINE WARREN, F.G.S.

*The Elephas-antiquus Bed of Clacton-on-Sea (Essex), and its Flora and Fauna*, by SAMUEL HAZZLEDINE WARREN, F.G.S.

The two papers were followed by discussions.

#### ROYAL SOCIETY OF ARTS.

The Cantor Lecture (3), entitled *Accurate Length Measurement*, was read on Monday, March 19, by J. E. SEARS, JUN., C.B.E., M.A., M.I.M.E., Assoc.M.INST.-C.E., Superintendent of Metrology Dept., National Physical Laboratory.

At the Ordinary Meeting on Wednesday, March 21, a paper entitled *Some Curious Phenomena of Vision, and their Practical Importance*, was read by F. W. EDRIDGE-GREEN, C.B.E., M.D., F.R.C.S., Special Examiner and Adviser of the Board of Trade on Colour-Vision and Eyesight. The paper was illustrated with lantern and other demonstrations. Professor E. H. Starling, C.M.G., M.D., Sc.D., F.R.S., presided.

#### THE CHEMICAL SOCIETY.

The Annual General Meeting of the Chemical Society was held on Thursday, March 22.

##### BUSINESS.

The Report of the Council for the year

ended December 31, 1922, was received and adopted.

The President, Sir James Walker, D.Sc., F.R.S., delivered his Presidential Address, entitled *Symbols and Formulæ*.

#### THE OPTICAL SOCIETY.

A meeting was held at the Imperial College, Imperial Institute Road, South Kensington, at 7.30 p.m. on Thursday, March 22, 1923, when the fifth of the series of lectures dealing with the evolution and development of optical instruments was delivered.

Subject: *Surveying and nautical instruments from a historical standpoint*. Lecturer: DR. I. C. MARTIN.

The lecture was illustrated by exhibits from the collection in the Science Museum, Kensington (by the kind permission of the Director, Col. Lyons, F.R.S.).

#### SOCIETY OF GLASS TECHNOLOGY.

A meeting of the Society was held in the Latin Theatre, The University, Edmund Street, Birmingham, on Wednesday, March 21, 1923.

The following papers were read and discussed:—

*A Rapid Method of Testing the Durability of Glassware*, by H. S. BLACKMORE, VIOLET DIMBLEBY, B.Sc., and PROF. W. E. S. TURNER, D.Sc.

*The Corrosion of Fireclay Refractory Material by Glass and Glass-making Materials*, by DONALD TURNER, B.Sc.TECH. (Lately Salter's Research Fellow), and PROF. W. E. S. TURNER, D.Sc.

*The Effect of Saltcake in Corroding Fireclay Materials*, by EDITH M. FIRTH, B.Sc., F. W. HODKIN, B.Sc., and PROF. W. E. S. TURNER, D.Sc.

By the courtesy of the directors, a visit was made to the works of Messrs. Austin Motor Co., Ltd., Northfield, Birmingham.

##### "DIRECTORY FOR THE BRITISH GLASS INDUSTRY."

This Directory, the publication of which has been unavoidably delayed, will be ready on March 20. It is bound in cloth and contains 384 pages. It may be purchased by members at the very low price of 6s., post free. Members who have not yet ordered a copy should send their order, with remittance, to the Secretary, Society of Glass Technology, Darnall Road, Sheffield.

## THE ESTIMATION OF LACTOSE.

By VINCENT EDWARDS, F.I.C.

The determination of milk sugar in various milk products has for many years past been carried out by Fehling's well-known method either volumetrically for O'Sullivan's weight method if the amount large percentages, or by modification of was small. There can be no doubt that with certain precautions and experience a rapid and accurate estimation can be made volumetrically, and as the subject is of increased interest owing to the proposed new regulations concerning "total solids" in milk, I venture to put forward a slight modification of the method which I have found useful as giving a much clearer indication of the end of the reaction, the obscurity of which has always been one of the drawbacks of this historic procedure.

I take 10 cc. of milk or other liquid milk product, or one gram of milk powder, dissolve in hot water, make up to nearly 100 cc., and boil with a few cc. of 10 per cent. acetic acid; allow to cool, dilute to 100 cc., filter off the casein; a perfectly clear filtrate should result. Ten cc. of mixed Fehling solution are now run into a small porcelain dish, and before dilution with 40 cc. of distilled water, a pinch (about sufficient to go on the point of a knife) of magnesium tartrate is mixed in. This valuable improvement is due to the late S. A. Vasey. The red precipitate is collected in the centre of the dish, with a ring of clear liquid round the sides, in which the blue colour is seen quite plainly.

My modification is in the subsequent stages. A piece of pure paraffin wax, about the size of a walnut, is put in the dish, the titration is then continued with the usual precautions, and with the additions mentioned a much better end indication can thus be obtained. If a slight excess, about 0.5 cc., of the test solution or a little more is run in, and allowed for, the clear yellow tinge showing the complete absence of copper in the solution is very apparent. As 10 cc. or one gram of the milk product is taken, the calculation of the result is quite simple, the factor 0.72 being taken for milk sugar. It is to be desired that in place of the term, "total solids," fuller particulars were given of the ingredients of milk. The public are becoming aware that the fat is not the only constituent worth consideration, and that proteins, sugar and phosphates have their own special value for dietetic purposes.

## CORRESPONDENCE.

## PROJECTED COMPENDIUM ON COLLOID CHEMISTRY.

To the Editor of THE CHEMICAL NEWS.

SIR,—With the assistance of prominent specialists the world over, I am preparing a comprehensive book on Colloid Chemistry, Theoretical and Applied. The extensive and international character of the book is evidenced by the list of those who have already promised contributions.

Many unusual experimental facts and practical applications of colloid chemistry principles are unpublished, and the object of this letter is to ask anyone in any field of science or experience, who may have information of interest, to send me a brief statement for inclusion in the book.

Contributions may consist of a paragraph, a page, or several pages, and will (unless contrary request is made) be duly acknowledged. If possible, they should be submitted in English, and duplicate copies will be appreciated. Authors should state their full names and titles.

The editors of scientific, technical and cultural publications in all countries are asked to disseminate this appeal.—Yours, etc.,

JEROME ALEXANDER, M.Sc.

50, East 41st Street, New York, U.S.A.

February 10, 1923.

[A long list of distinguished chemists and scientists of all countries, who have contributed to the knowledge of colloid chemistry, is appended.—Ed., C.N.]

## THE AUTHENTICITY OF THE LATIN WORKS OF GEBER.

To the Editor of THE CHEMICAL NEWS.

SIR,—I was much interested to read Mr. E. E. Whale's letter on the above topic, in your issue for March 9, and the excellent report of Mr. Holmyard's lecture on "Arabian Alchemy and Chemistry," which appeared in the previous issue. In that report you were kind enough to include my own remarks—to which I would draw Mr. Whale's attention—which perhaps sufficiently define my own position towards the question of Geber in the light of Mr. Holmyard's researches; but it may possibly be of use if I briefly expand these here. Like Berthelot, I know no Arabic, and in common with him and other writers

on the history of chemistry, I had to rely, when writing *Alchemy: Ancient and Modern*, upon the translations of Geber's original works, which Berthelot had had prepared for the purposes of his own studies. Judging from these, no other conclusion seemed possible than would appear to be that for adequate translations of these Arabic MSS., and it is to be hoped that Mr. Holmyard might be persuaded to undertake this important work. A translation of Geber's *Book of Properties*, for example, the MSS. of which is in the British Museum, would be especially welcome. Until such translations have been made it may be as well to retain an open mind concerning the question of the authenticity of the Latin works; but certainly the evidence for reversing the decision, arrived at by Berthelot, which Mr. Holmyard has already put forward is, to my mind, very convincing.

As to the different spellings, "Geber" and "Dschabir," these are merely different transliterations of the same Arabic name, and do not refer to different individuals.—Yours, etc.,

H. STANLEY REDGROVE,  
B.Sc., A.I.C., F.C.S.

191, Camden Road, N.W.1.  
March 10, 1923.

#### BOOKS RECEIVED.

*A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, by J. W. MELLOR, D.Sc. Pp. X. + 927. Vol. III., 1923. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 63s. net.

*Anorganische Chemie*, by DR. FRITZ EPHRAIM. Pp. VIII. + 742. 1923. Verlag von Theodor Steinkopff, Dresden and Leipzig. 8s. 6d., Bound 10s. 2d.

*Glue and Gelatin*, by JEROME ALEXANDER. Pp. 236. 1923. The Chemical Catalog Co. Inc., 19, East 24th Street, New York, U.S.A. 3 dollars.

*Chemical Technology and Analysis of Oils, Fats and Waxes*, by DR. J. LEWKOWITSCH, M.A., F.I.C. Entirely revised by GEORGE H. WARBURTON. Pp. VIII. + 508. Sixth Edition. Vol. III. 1923. Messrs. Macmillan & Co., Ltd., St. Martin's Street, W.1. 36s. net.

*Vital Factors of Foods, Vitamins and Nutrition*, by CARLETON ELLIS, S.B., F.C.S., and ANNIE LOUISE MACLEOD, PH.D.

Pp. XIII. + 391. 1923. Messrs. Chapman & Hall, Ltd., 11, Henrietta Street, Covent Garden, W.C.2. 25s. net.

*The Mathematical Theory of Relativity*, by AUGUST KOPFF. Translated by H. LEVY, M.A., D.Sc., F.R.S.E. Pp. VIII. + 214. 1923. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C.2. 8s. 6d. net.

*The Chemists' Year Book*, by F. W. ATACK, assisted by L. WHYNATES, A.M.C.T., A.I.C. Pp. 1,107. Vols. I. and II. 1923. Messrs. Sherratt & Hughes, 34, Cross Street, Manchester. £1 1s. 9d. (Abroad, £1 2s.).



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

5027—Carmichael, Co., Ltd., J. F.—Means for elevating and controlling supply of acids, etc. Feb. 21.

4965—Durand et Huguenin Soc. Anon.—Manufacture of highly chlorinated hydro-aromatic products containing nitrogen. Feb. 20.

4873—Lamoreaux, W. F.—Manufacture of sulphuric acid. Feb. 20.

5374—Margulies, O.—Production of organic arsenic compounds. Feb. 23.

5308—National Benzene Association.—Process of treating aromatic hydrocarbons. Feb. 23.

4837—Pickett, F. N.—Method of removing chloropierin from stannic chloride pentahydrate solution. Feb. 19.

#### Specifications Published this Week.

170302—Chemische Fabriken Vorm.—Process of purifying natural cellular structures containing xanthine derivatives.

192778—Pease, E. L.—Production of material suitable for use as a fertiliser

192842—Akt Ges für Anilin Fabrikation.—Manufacture of new dyestuffs.

192941—Byrom, J. G., and Attwater, R.—Method of manufacturing formaldehyde condensation products of phenols.

192970—Goldschmidt, H., and Stock, A.—Process for electrolytically manufacturing compact metallic beryllium.

191029—Etablissements Poulenc Freres and Oetehslin.—Manufacture of aliphatic arsenical compounds.

#### Abstract Published this Week.

191305—Dyes.—Soc. of Chemical Industry in Basle; Basle, Switzerland. Basle, Switzerland.

Monoazo dyes, yielding fast violet-blue to brown shades when chrome printed on cotton are obtained by coupling diazotized 1-amino-2-oxynaphthalene-4-sulphonic acid, or a substitution product thereof, with B-resoreylic acid; in examples the diazo compound itself and the nitrated diazo compound are used.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3285.

## A NEW DISTINCTION BETWEEN SODIUM AND POTASSIUM.

By C. W. L. BOURLET AND W. THOMAS.

The elements, sodium and potassium, are so much alike chemically that any point of marked difference between them seems worthy of note.

The following facts, which, so far as we know, are brought forward for the first time, point to a highly interesting difference in the colloidal constitution of the aqueous solutions of the fatty acid salts of potassium and sodium.

It is common knowledge that solutions of sodium oleate of higher concentration than 5 per cent. form a gel on cooling to normal temperatures. Solutions of potassium oleate, on the other hand, may be poured from one vessel to another till the concentration reaches approximately 40 per cent. In the case of the potassium soaps the change of concentration *gradually* increases the viscosity till the mass becomes very viscous, and finally plastic.

In the case of the sodium soaps, however, the change from sol to gel is sudden: slight variations in concentration or temperature induce enormous variations in viscosity.

The addition of phenol or cresol to a potassium soap solution "thickens" it, *i.e.*, the viscosity is increased, the effect being most marked in the case of phenol.

In the case of the sodium soap, however, the effect is reversed: phenols partially destroy the power of gel formation and lower the viscosity. Thus, the addition of 4 per cent. phenol or 2½ per cent. of *o*, *m*, or *p*-cresol to a 10 per cent. solution of sodium soap reduces it to a liquid comparable in viscosity with water at ordinary temperatures. Super-cooling causes it to gel at a lower temperature, depending on the concentration of soap and phenol. Gel formation, however, is always *sudden*; there is no gradual increase in viscosity as in the case of a potassium soap. The addition of sodium hydroxide, carbonate, or silicate in sufficient quantities restores the power of gel formation.

To distinguish between a potash and a soda "soft" soap, it is only necessary to

prepare a 15 per cent. aqueous solution, measure the efflux time at constant temperature from a pipette; then add (say) 4 per cent. phenol. In the case of a potash soap the efflux time will be increased; in the case of a soda soap, decreased.

## VALENCY.

By WILLIAM R. FIELDING, M.A., M.Sc.,  
(VICT.).

Senior Science Master, King Edward VII.  
School, Lytham.

(Continued from Page 180.)

### (8) MANIFESTATIONS OF VALENCY.

Valency is manifest in different ways, and it is impossible to differentiate between the different "kinds," if any difference exists. It is a force holding two portions of matter together.

1.—*Valency of Atomic Structure*, holding the positive nucleus and the electrons together. As an atom loses or gains an electron its valency is increased by one unit.

2.—There is molecular valency

(a) holding the atoms in an elementary molecule together;

(b) holding unlike atoms together in chemical combination.

3.—Polymolecular valency holding two or more like molecules together.

4.—Valency of aggregation, holding a number of molecules together in an aggregation (see *The Chemical News*, 1920, CXX., 3136; CXXII., 3170).

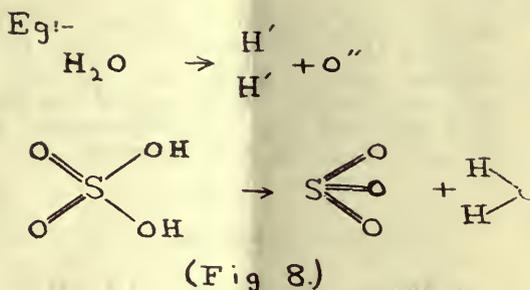
5.—Valency of Cohesion (holding like aggregations together), and adhesion (unlike aggregations).

6.—Valency of solution. This subject will be dealt with in a subsequent article.

Valencies 3, 4, 6 rapidly change with temperature (see *The Chemical News*, 1921, CXXII., 13, 289, etc.).

### (9) WHEN TO COMPARE VALENCIES.

We ought, if possible, to compare the valencies of elements (No. 2 above), under the same conditions, say, either at the B.P. or just at the moment of decomposition.



This would lead us to form a table of valencies like the following:—

Elements.	Valency.
H	1
O	2 (H <sub>2</sub> O)
S	4 (SO <sub>2</sub> )
C	4 (CH <sub>4</sub> , CO <sub>2</sub> )
P	3 (PCl <sub>3</sub> )
Hg	2 (HgO)

A complete table could only be compiled from data obtained from compounds which can be vapourised without decomposition. No account would be taken of "residual" or "supplementary" valencies (which might exist), but we should at least be consistent.

#### (10) PERIODICITY OF VALENCY.

Certain elements which are diatomic in the gaseous state have come to be regarded as monovalent or standard elements.

H — H, F — F, Cl — Cl, H — Cl.

Also certain radicles which exist in the "paired" state:—



Also note  $\begin{array}{c} \text{C}_2\text{H}_5 \\ | \\ \text{H} \end{array}$   $\begin{array}{c} \text{H} \\ | \\ \text{OH} \end{array}$  etc.

The highest valencies are shown by elements in their oxides (as usually written in their graphical formulæ). From the oxide X<sub>x</sub>O<sub>y</sub> the valency (which may be as high

as 8) is  $\frac{2y}{x}$

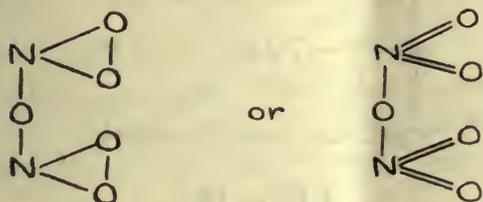
The highest valencies obtained by different methods are shown below for two series of the periodic table (Fig. IX.).

GROUPS:—	0	I	II	III	IV	V	VI	VII	VIII
Valency from	He	Li	Be	B	C	N	O	F	—
Oxides:—	0	1	2	3	4	5	—	—	—
Hydrides and Radicles:—	0	—	—	—	4	3	2	1	—
Hydroxides:—	0	1	2	3	4	HO(NO <sub>2</sub> )	—	—	—
Halides:—	0	1	2	3	4	3	2	1	—
Valency from	Ne	Na	Mg	Al	Si	P	S	Cl	—
Oxides:—	0	1	2	3	4	5	6	7	OsO <sub>4</sub>
Hydrides and Radicles:—	0	1	2	3	4	3	2	1	—
Hydroxides:—	0	1	2	3	4	P(OH) <sub>3</sub> 3	SO <sub>2</sub> (OH) <sub>2</sub> 2	ClO <sub>3</sub> (OH) 1	—
									—
Halides:—	0	1	2	3	4	5	4	—	—

HIGHEST VALENCY TABLE: (Periodic Series He and Ne).

(Fig IX.)

Frequently an element does not reach as high a valency in one compound as in another, although it is surprising how many of these cases can be explained away by the simple process of valency bonds (Fig. X.):—

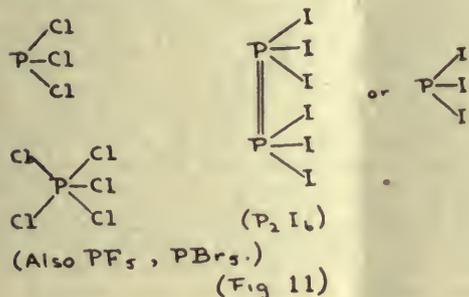


(Fig 10)

In  $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ ,  $\text{HClO}_4$  chlorine is gradually climbing to its maximum valency (7).

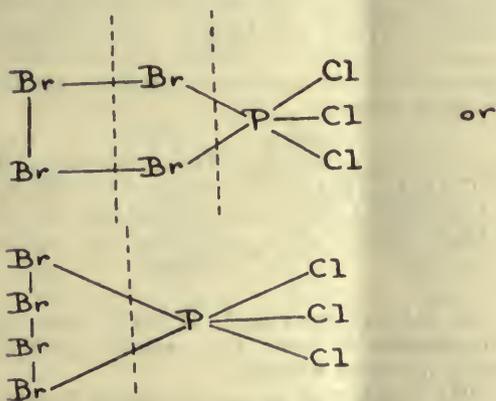
Iron is dyad in  $\text{FeO}$ ,  
 triad in  $\text{Fe}_2\text{O}_3$ ,  
 tetrad in  $\text{Fe}_3\text{O}_4$  ( $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ ).

The phosphorus compounds with the halogens show the following valencies (Fig. XI.):—



(Fig 11)

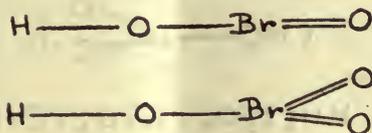
In the crystalline mixed halide,  $\text{PCl}_3 \cdot \text{Br}_3$ , phosphorus has a still higher valency unless we write it



(Fig 12)

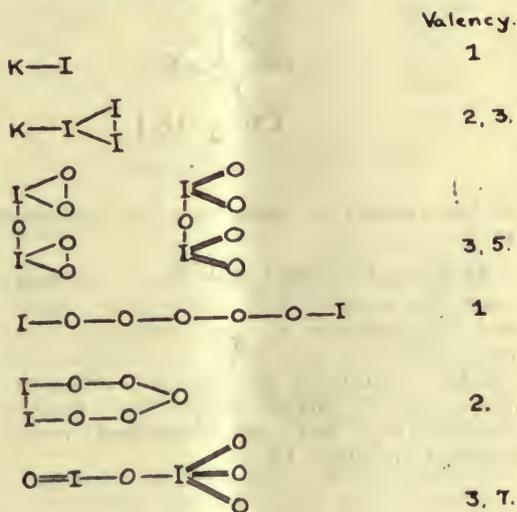
the dotted lines showing the points where decomposition readily occurs (the weak links).

Here bromine would be dyad. Also note



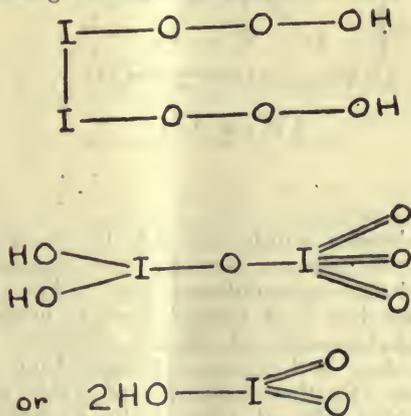
(Fig 13.)

Iodine can be conveniently given any valency between 1 and 7. Thus:—



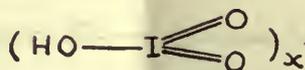
(Fig 14)

Adding a molecule of water we get

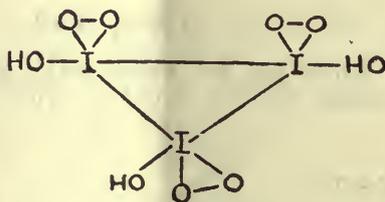


(Fig 15.)

The acid iodates may be regarded as as derived from



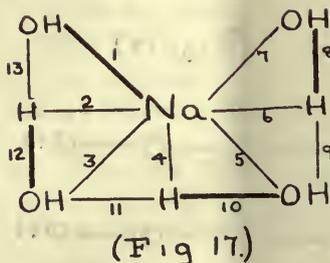
eg.:—  $\text{KH}_2\text{I}_3\text{O}_9 (\text{KIO}_3 \cdot 2\text{HIO}_3)$ ;



(Fig 16.)

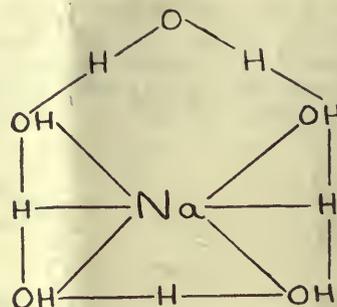
or the valency of iodine may be increased to 7.

Mendeléef pointed out that in many cases the sum of the valencies in oxides and hydrides was 8, and attempts have been made to give such low-valent elements as sodium a valency of 7. The hydrate  $\text{NaOH} \cdot 3\text{H}_2\text{O}$  may be written  $\text{Na}(\text{OH})_4\text{H}_3$ , and the compound represented thus (Fig. 17):



(Fig 17.)

Valencies numbers 1, 12, 10, 8, are in the first instance strong; the remainder "residual" or supplementary. After the hydrate has been formed there is probably a redistribution of valency-strength, but these four will remain stronger than the others. Further molecules of water could be added without altering the heptavalent character of the sodium, thus:—



(Fig 18)

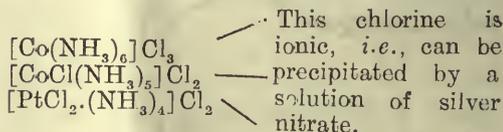
(Note.—There should be a bond between Na and the lowest H.)

The valency of hydrogen is more than one, but it can be reduced to 2 by cancelling bonds 9, 11, 13.

#### (11) THEORIES OF VALENCY.

It would be impossible in the space of a short article to refer to the many different and often ingenious theories put forward to explain the phenomenon of valency.

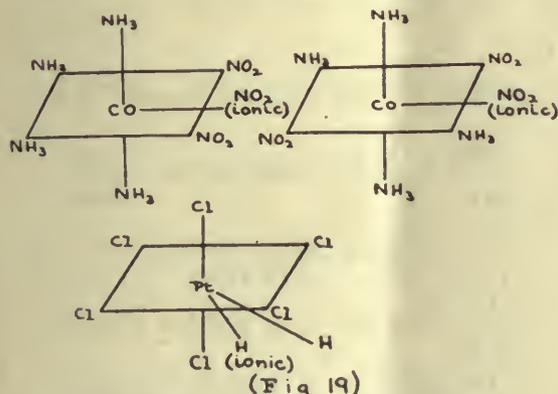
Probably Werner's theory is the one most widely held to-day. Werner supposed that atoms could be connected to each other in two ways, directly and indirectly by the existence of a force which is able to penetrate the envelope of protective atoms or groups which surround the central atom. The latter is directly united with the non-ionisable groups, such as  $\text{NH}_3$ ,  $\text{NO}_2$ , which are included in the complex radicle and they are not ionised in solution. The valencies so employed are termed the supplementary valencies of the central metal. The principal valencies are used to link on to ionisable groups. These ionisable groups are outside the complex formed through the agency of the supplementary valencies. Werner put the ionisable part of the molecule outside a square bracket, thus:—



In chloroplatinic acid,  $\text{H}_2\text{PtCl}_6$ , none of the chlorine is ionic, i.e., can be precipitated by silver nitrate.

The number of groups or atoms directly bound to the central atom (in the above cases) is 6; this is termed the "co-ordina-

tion number"—“ a fundamental property of the elementary atom.” This theory predicted and explained the existence of isomers, many of which have been since isolated. Where the co-ordination number is 6 the groups can be represented at the angles of a regular octahedron, thus:—



A recent writer has said: “It must be admitted that the conceptions used in Werner’s theory, e.g., those of ‘supplementary valencies’ and of the ‘positions inside and outside the nucleus’ are vague,” and the author has, he believes, discovered an alternative method of explaining the formation of these complex molecules. Several compounds were examined with the object of finding out, whether, if  $p$  and  $p_1$  are the rates of polymerisation of the component parts of a compound and  $A$  and  $B$  the percentage composition,

$$\frac{pA + p_1B}{100} = p_2,$$

where  $p_2$  is the rate of polymerisation of the compound (see *The Chemical News*, 1921, CXXII., 3170).

*Lead Sulphide.*

	Temp. (A°)	p	
Pb	307	1.47	} Calculated from specific heats.
S (rhombic)	304	1.83	
PbS	305	1.62	

	Percentage.	p.	p x %
Pb	86.6	1.47	127.3
S	13.3	1.83	24.3

Average  $p = 1.516$   
Observed  $p = 1.62$

BaCl <sub>2</sub> . 2H <sub>2</sub> O.				
BaCl <sub>2</sub>	329	1.59		
2H <sub>2</sub> O	273	3		(Considered as trihydrol)

BaCl <sub>2</sub> . 2H <sub>2</sub> O	305	2.05		
	%	p	% x p	
BaCl <sub>2</sub>	85.2	1.59	135.5	
2H <sub>2</sub> O	14.8	3	44.4	
			179.9	

Average  $p = 1.8+$   
Observed  $p = 2.05$  At 305°

<u>CuSO<sub>4</sub> . 5H<sub>2</sub>O.</u>		T	%	p	p x %
CuSO <sub>4</sub>	335	63.8	2+	127.6+	
5H <sub>2</sub> O	273	36.2	3	108.6	
				236.2	

Average  $p = 2.36+$   
Observed  $p = 2.61$  (335°)

<u>Mg(OH)<sub>2</sub>.</u>		T	%	p	p x %
MgO	335	71.4	2.01	143.5	
H <sub>2</sub> O	273	28.6	3	85.8	
				229.3	

Average  $p = 2.29$   
Observed  $p = 2.65$  (at 308°)

The value of  $p$  for solid water is reckoned as 3 (its value at 273°), and so the average value of  $p$  would be lower in every case, and the disparity between the “average” and the “observed” values greater.

(To be Continued.)

THE LAW OF MAGNETIC ROTATION.

By HAWKSWORTH COLLINS.

The magnetic rotation of an electro-positive element, when in combination, is the product of half its atomic weight and the reciprocal of its relative volume.

The observation of this law rests not only upon the data given below, but also upon a very large number of facts arranged in a particular manner, which is called “The Correlation of Physico-Chemical Constants.”

Earlier papers concerning the Heat of Formation of molecules were published in *The Chemical News* of August 18 and 25, 1922. The publication of the whole matter concerning these constants was commenced by *The Chemical News* on January 7, February 11 and 18, and August 19, 1921.

Table I. gives the relative volumes of the elements concerned. Table II. gives all available experimental results by Perkin in magnetic rotation; excluding compounds in which hydrogen occurs, for these cannot be included in a short paper. Table III. demonstrates the law.

TABLE I.

	Relative Volume.	Theor. S.G.	Obs. S.G. & Observer.
CaCO <sub>3</sub>	13.25 + 20.55 = 33.8	100 — = 2.959	2.938—2.995 Breithaupt
CaO	13.25 + 4.45 = 17.7	33.8 56 — = 3.164	3.161 Karsten 3.18 Filhol
CaCl <sub>2</sub>	13.25 + 2(15.085) = 43.42	17.7 111 — = 2.56	2.48 Playfair & Joule
CaBr <sub>2</sub>	12.24 + 2(23.09) = 58.42	43.42 198 — = 3.39	3.32 11° Bodeker
CaS	12.24 + 15.53 = 27.77	58.42 72 — = 2.59	2.58 Maskelyne
BaCl <sub>2</sub>	24.0 + 2(15.085) = 54.17	27.77 207 — = 3.82	3.82 Schiff
BaBr <sub>2</sub>	24 + 2(23.09) = 70.18	54.17 296 — = 4.22	4.23 Schiff
CdCl <sub>2</sub>	14.57 + 2(15.085) = 44.74	70.18 182 — = 4.07	4.05 25° Van Nostrand
CdBr <sub>2</sub>	14.57 + 2(23.09) = 60.75	44.74 271 — = 4.46	4.712 14° Bodeker
CdI <sub>2</sub>	14.57 + 2(27.73) = 70.03	60.75 365 — = 5.21	5.543 Kebler 4.576 10° Bodeker
CdO	15.16 + 2.51 = 17.67	70.03 127 — = 7.19	8.11 Werther 6.95 Karsten
CdSO <sub>4</sub>	15.16 + 15.53 + 2(7.53) + 2(2.51) = 50.77	17.67 207 — = 4.08	4.447 Schroder
SrCl <sub>2</sub>	23.96 + 2(15.085) = 54.13	50.77 159 — = 2.94	2.960 Filhol 2.8033 Karsten
SrCO <sub>3</sub>	19.56 + 20.55 = 40.11	54.13 148 — = 3.69	3.68—3.714 Dana
SrI <sub>2</sub>	19.56 + 2(27.73) = 75.02	40.11 342 — = 4.56	4.55 25° Van Nostrand
SrBr <sub>2</sub>	19.56 + 2(23.09) = 65.74	75.02 248 — = 3.77	3.962 12° Bodeker
		65.74	

LiCl	$6.21 + 15.085 = 21.295$	$\frac{42.5}{21.295} = 1.996$	1.998 Kremers
Li <sub>2</sub> S	$2(6.21) + 15.53 = 27.95$	$\frac{46}{27.95} = 1.646$	1.63—1.7 Van Nos-trand
Li <sub>2</sub> SO <sub>4</sub>	$2(6.21) + 15.53 + 2(7.53) + 2(2.51) = 48.03$	$\frac{110}{48.03} = 2.29$	2.21 15° Brauner
NaCl	$11.85 + 15.085 = 26.935$	$\frac{58.5}{26.935} = 2.17$	2.17 20° Kaye & Laby
NaBr	$11.85 + 23.09 = 34.94$	$\frac{103}{34.94} = 2.95$	2.952 Schiff
Na <sub>2</sub> CO <sub>3</sub>	$2(11.85) + 20.55 = 44.25$	$\frac{106}{44.25} = 2.40$	2.407 Favre
NaI	$11.85 + 27.73 = 39.58$	$\frac{150}{39.58} = 3.79$	3.654 18° Favre
KCl	$22.29 + 15.085 = 37.375$	$\frac{74.5}{37.375} = 1.994$	1.994 Filhol
KBr	$22.29 + 23.09 = 45.38$	$\frac{119}{45.38} = 2.62$	2.672 P & J 2.505 18° Spring
K <sub>2</sub> SO <sub>4</sub>	$2(18.05) + 15.53 + 2(7.53) + 2(2.51) = 71.71$	$\frac{174}{71.71} = 2.43$	2.4073 Hassenf 2.572 Buignet
K <sub>2</sub> S	$2(18.05) + 15.53 = 51.63$	$\frac{110}{51.63} = 2.130$	2.130 Filhol

TABLE II.

	Theoretical Magnetic Rotation.		M.R. by Perkin.
CaCl <sub>2</sub>	$1.51 + 2(3.932)$	$= 9.374$	9.38
CaBr <sub>2</sub>	$1.635 + 2(7.95)$	$= 17.535$	17.6
BaCl <sub>2</sub>	$2.833 + 2(3.932)$	$= 10.967$	10.08
BaBr <sub>2</sub>	$2.833 + 2(7.95)$	$= 18.733$	18.54
CdCl <sub>2</sub>	$3.81 + 2(3.932)$	$= 11.674$	11.78
CdBr <sub>2</sub>	$3.81 + 2(7.95)$	$= 19.71$	19.7
CdI <sub>2</sub>	$3.81 + 2(18.32)$	$= 40.45$	40.8
CdSO <sub>4</sub>	$3.66 + 1.03 + 2(0.042) + 2(0.202)$	$= 5.178$	5.17
SrCl <sub>2</sub>	$1.836 + 2(3.932)$	$= 9.7$	9.7
SrBr <sub>2</sub>	$2.25 + 2(7.95)$	$= 18.15$	18.16
LiCl	$0.564 + 3.932$	$= 4.5$	4.61
Li <sub>2</sub> SO <sub>4</sub>	$2(0.564) + 1.03 + 2(0.042) + 0.202$	$= 2.646$	2.27
NaCl	$0.97 + 3.932$	$= 4.902$	5.068
NaBr	$0.97 + 7.95$	$= 8.92$	9.19
NaI	$0.97 + 18.32$	$= 19.29$	18.46
NaCO <sub>2</sub> CH <sub>3</sub>	$0.97 + 2.299$	$= 3.269$	3.281
NaCO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	$0.97 + 2.299 + (1.023)$	$= 4.292$	4.308
NaCO <sub>2</sub> C <sub>3</sub> H <sub>7</sub>	$0.97 + 2.299 + 2(1.023)$	$= 5.315$	5.332
KCl	$1.749 + 3.932$	$= 5.681$	5.66
KBr	$1.749 + 7.95$	$= 9.699$	9.36
KI	$1.08 + 18.32$	$= 19.4$	18.95
K <sub>2</sub> SO <sub>4</sub>	$2(1.08) + 1.03 + 2(0.042) + 0.202$	$= 3.678$	3.57

LiNO<sub>3</sub> is the only other available compound. Its M.R. is given as "1.124 and higher."

The experimental data for the magnetic rotation are always dependent upon the specific gravity. By employing a slightly different value from that which was probably used, the experimental figures can in nearly every case be brought exactly to the theoretical figures. For instance, the following are given as the S.G. of  $\text{BaCl}_2$  :—

3.82 Schiff  
3.860—4.156 Boullay.

Suppose 4.056 was employed as the S.G. If 3.82 had been used instead, the result would have been

$$\frac{10.08 \times 4.056}{3.82} = 10.697$$

TABLE III.  
Calcium.

$$\frac{40}{\quad} = 1.51$$

$$\frac{2 \times 13.25}{\text{Calcium. } 40} = 1.635$$

$$\frac{2 \times 12.24}{\text{Barium. } 136} = 2.833$$

$$\frac{2 \times 24}{\text{Cadmium. } 111} = 3.81$$

$$\frac{2 \times 14.57}{\text{Cadmium. } 111} = 3.66$$

$$\frac{2 \times 15.16}{\text{Strontium. } 88} = 1.836$$

$$\frac{2 \times 23.96}{\text{Strontium. } 88} = 2.25$$

$$\frac{2 \times 19.56}{\text{Lithium. } 7} = 0.564$$

$$\frac{2 \times 6.21}{\text{Sodium. } 23} = 0.97$$

$$\frac{2 \times 11.85}{\text{Potassium. } 39} = 1.08$$

$$2 \times 18.05$$

In addition to these results concerning electro-positive elements, the non-metallic element sulphur gives—

Sulphur.

32

$$\frac{\quad}{\quad} = 1.03$$

$$2 \times 15.53$$

and potassium gives another result, which differs from the others in not having its atomic weight halved :—

Potassium.

39

$$\frac{\quad}{\quad} = 1.749$$

$$22.29$$

If in the future any results similar to the last can be demonstrated, it will of course be evident that there is no discrepancy in the matter, but that the exceptions only lead to a deeper truth.

As the atomic numbers are sometimes stated to be rather less than half the atomic weights, it seems possible that with more accurate experimental data, the law may in the future be stated as follows :—  
“The magnetic rotation of an electro-positive element, when in combination, is the product of its atomic number and the reciprocal of its relative volume.”

The two values 4.45 and 2.51 for oxygen, given in the relative volumes, are supported exactly by the Heats of Formation of the two substances  $\text{CaO}$  and  $\text{CdO}$  as published in *The Chemical News*, August 18, 1922.

#### A NEW METHOD OF DETECTING NICKEL IN SOLUTION.

By C. G. VERNON, B.A., B.Sc.

Concentrated ammonia in excess was added to the solution containing nickel, and hydrogen sulphide was passed through for a short time.

The solution was then boiled.

A *bright mirror* of metallic nickel was deposited, and its production was accompanied by a blackening of the solution.

This has been shown to occur even in very dilute solutions. If only a small trace of nickel was present the mirror took the form of an iridescent film.

Since the presence of cobalt does not affect it, the test is of some use in detecting nickel when mixed with cobalt. It may be introduced into the ordinary course of qualitative analysis by adding excess of strong ammonia before passing in hydrogen sulphide to precipitate the sulphides of the metals in the nickel group.



## GENERAL NOTES.

GERMANY'S TRADE AND INDUSTRY  
IN FEBRUARY.

The Commercial Secretary at Berlin, Mr. J. W. F. Thelwall, has forwarded a report on the state of trade and industry during February.

The report states that in spite of the cutting off of the industrial west from the remainder of Germany, it has, in general, been possible to maintain industry in the Ruhr district and on the Rhine, as also in the rest of Germany. Ruhr coal, so far as not required within occupied territory, is being accumulated at the pit dumps and in the depots of the large works. The non-delivery of reparation coal to France and Belgium practically makes good the reduction of output which has naturally taken place since the occupation. Unoccupied Germany is helping itself by means of increased production and larger imports, above all, of English coal, so that the demand can be covered. It was endeavoured to make up for the shortage of pig iron, firstly, by an increased production of this material in Upper Silesia; finished iron was also delivered on a large scale thence, while the occupied territory had, to a large extent, to work on stock.

**Potash.**—In spite of the occupation of the Ruhr, the full maintenance of the potash industry was possible. Only comparatively small quantities of individual goods were stored. The sale of potash raw salts have, however, again fallen off as a result of increased railway freights, the latter already far exceeding the value of the goods. The call for by-products of the potash industry was only partially satisfactory; considerable quantities of sulphate of potash were, however, exported to the United States.

**Aluminium.**—In the Lüdenscheld aluminium and finished metal-goods industries, employment was bad, and the outlook for the future is not at all favourable. The industries are suffering from diminished foreign sales, and consequently the removal of the export duty and of foreign trade control is more than ever urgently desired.

**Electrical Industry.**—In the electrical industry the inland purchasing power is still weak. Neither official nor private

customers dare place orders for large plant and machinery. Further, the partial fall of prices is causing some customers to hold back in the hope of further reductions. Foreign countries are, for the most part, showing reserve, in so far as the German prices, which have partly reached the world's market level and partly already exceeded it, admit of any competition. Accordingly a general falling off in orders is noticeable in high pressure current articles, machinery, apparatus, calculators, installation materials and cables. With regard to measuring instruments and electro-medical apparatus, the position is no better, owing to customers' loss of purchasing power. The outlook for railway safety appliances is bad. The sale of electric lamps at home and abroad shows no improvement.

**Chemical Industry.**—No details are available with regard to the chemical industry in the occupied territory. In general, however, it may be said that the chemical industry of the south portion of the occupied territory is suffering from a scarcity of coal. In the northern portion conditions are better. No restrictions of work have yet taken place. The hourly wage for unskilled workers is now 1,780 marks.

**Glass Industry.**—In the sheet glass industry very few inland orders were received. The general export figure remained unaltered. The works which deliver to the Russian border States lost practically their whole market as a result of cheaper offers from the Czecho-Slovakian glass industry. In the hollow-glass industry the supply of raw materials, with the exception of soda, was adequate.

**Mining Industry.**—The events in the Ruhr district accentuated the importance of Upper Silesian pit coal for the coal supply of the country. The Coal Commissioner of the Reich drew larger supplies of such coal for despatch to South Germany and Saxony, at the same time partly diverting Upper Silesian coal from the coastal districts, as these are better able to obtain supplies of English coal. Besides English coal, the import of coal from the Ostrau mines, which is particularly suitable for use in gasworks, has begun.

## MEDICAMENTS FOR BULGARIA.

The Bulgarian Government invites tenders for adjudication on the 16th April for the supply of various medicaments, a list

of which is available for inspection at the Department of Overseas Trade by firms interested.

Local representation is essential. Firms desirous of tendering, but not locally represented, will be furnished upon application to the Department with the names of suitable firms.

#### OILS, PAINTS AND VARNISHES FOR EGYPT.

The British Commercial Agent for Egypt reports that the Egyptian Government invite tenders for the supply of oils, paints, and varnishes. Tenders close on the 17th April, and local representation is essential. The Department of Overseas Trade will be pleased to supply firms desiring to tender, not locally represented, with the names of some United Kingdom houses with Egyptian connections open to handle tenders on behalf of third parties.

Copies of the specification and conditions of tender are available for inspection at this Department (Room 53).

#### CZECHO-SLOVAKIA.

##### DEMAND FOR BRITISH CHEMICALS.

The Commercial Secretary at Prague (Mr. W. F. Vaughan Scott) reports that up to the present no falling off in the imports of chemicals from Germany has been noticeable, but there is no doubt that, owing to the rapid increase in prices of all German chemicals, and to the difficulty which importers anticipate experiencing in obtaining delivery of goods, an increased demand is likely to arise for the following British chemicals:—

- Coal-tar and its derivatives.
- Resin.
- Cresines and petroleum jelly.
- Refined yellow and white beeswax.
- Oils for perfumes, soapmakers, and for medicinal purposes.

Pharmaceutical products.

Photographic chemicals.

Raw materials for the chemical industry.

The Commercial Secretary has also furnished (1) the names and addresses of agents who might suitably represent British firms of chemical manufacturers, and (2) a list of the most important Czecho-Slovak importers of chemicals. Copies of these lists may be obtained by interested United Kingdom firms upon application to the Department of Overseas Trade.

#### TRADE FAIRS.

##### ARE TRADE FAIRS AND EXHIBITIONS WORTH THE OUTLAY?

Last week's *Manchester Guardian Commercial* states that much energy and money must have been wasted on fair schemes, energy which, if only directed by intelligence instead of imagination, might have produced real results. Trade fairs generally fall under one of two heads, *Direct Business* and *Propaganda*. Under the former fall, those attended principally by "the trade," and at which actual orders from trade buyers are expected, the attendance of the general public is neither invited nor encouraged. The remainder come under the heading of *Propaganda*. With certain notable exceptions, the possibility of immediate business diminishes in proportion to the attendance of a merely curious public. Many of them undoubtedly are good value for the money demanded, either in publicity, in direct business, or in both combined. Firms taking part in these may receive a good return on the money paid for the space occupied. Few firms have a considered and definite policy in regard to exhibitions. Like any other medium of trade, an exhibition should be the subject of a definite policy, and each proposal should receive due consideration.

#### INDIAN IMPORTS FROM APRIL TO DECEMBER, 1922.

Mr. T. M. Ainscough, O.B.E., H.M. Senior Trade Commissioner in India, draws attention to the following features:—

The total imports of merchandise for the nine months declined somewhat. Shipments from the United Kingdom declined, but the British share of the total rose from 56 per cent. to 61 per cent. The most striking feature has been the increase in the proportion of goods derived from Germany, from 2.4 per cent. to 5 per cent.

There are good grounds for satisfaction that in a time of such depression the United Kingdom should be maintaining her position in the Indian import trade.

*Dyestuffs obtained from Coal Tar.*—The total trade fell from 207 to 189 lakhs. The British share was reduced from 58 to 15 lakhs, and that of America from 24 to 7 lakhs, but Germany, who once again controls this trade, increased her share from 92 to 146 lakhs.

*Coal*.—Although the total trade fell considerably, the reduction has mainly been in Natal, Portuguese East African, and Australian coal. The imports from the U.K. were reduced only slightly.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE ROYAL SOCIETY.  
THURSDAY, MARCH 22, 1923.

Papers read:—

L. T. HOGBEN and F. R. WINTON. *The Pigmentary Effector System. III.—Colour Response in the Hypophysectomised Frog.* Communicated by Prof. E. W. MacBride, F.R.S.

H. R. SEWER. *Studies on Amphibian Colour Change.* Communicated by Prof. E. W. MacBride, F.R.S.

J. WALTON. *On Rhexoxylon, Bancroft. A Triassic Genus of Plants exhibiting a Liane-type of Vascular Organisation.* Communicated by Prof. A. C. Seward, F.R.S.

Papers read in title only:—

G. HEWETT. *The Dusuns of British North Borneo.* Communicated by W. B. Hardy, Sec. R.S.

M. TRIBE. *The Development of the Hepatic Venous System and the Postcaval Vein in the Marsupialia.* Communicated by Prof. J. P. Hill, F.R.S.

J. GRAY. *The Mechanism of Ciliary Movement. III.—The Effect of Temperature.* Communicated by Prof. J. S. Gardiner, F.R.S.

E. PONDER. *The Inhibitory Effect of Blood Serum on Hæmolysis.* Communicated by Sir E. Sharpey Schafer, F.R.S.

ROYAL MICROSCOPICAL SOCIETY.

The section of the Society which has been formed to deal with the Industrial Applications of the Microscope, and to assist in the development of Industrial Research in British Industries, held a meeting at 20, Hanover Square, W.1, on Wednesday, March 28.

Messrs. J. W. Atha & Co. exhibited the new Zeiss Photographic Eye-piece, "Phoku."

Mr. John H. Barton exhibited a new Research Microscope of original design.

Messrs. R. & J. Beck, Ltd., exhibited a microscope specially suitable for the ex-

amination of large surfaces of paper and of prints and engravings.

The Edison Swan Electric Co., Ltd., demonstrated the Ediswan Pointolite Lamp, 30, 100, 500 and 1,000 c.p. in operation. They also exhibited and explained the working of the alternating current Pointolite lamp.

Messrs. Ogilvy & Co. exhibited a new stereoscopic magnifier giving large field of view and long working distance.

Mr. Mansell P. Swift demonstrator Professor Shand's recording micrometer which is designed to facilitate the quantitative estimation of minerals in rocks.

Communications.

Mr. J. LEONARD SPICER in the chair.

MR. JAMES STRACHAN, F.INST.P., F.R.M.S., *The Manufacture of Containers and Papers used for the wrapping of Food-stuffs.*

MR. HAROLD B. WRIGHTON, B.MET., F.R.M.S., *The Microscope in Metallurgical Research.*

MR. SYDNEY R. WYCHERLEY, F.R.M.S., *Microscopy in the Examination of Manufactured Paper.*

Future meetings, for which invitations may be obtained on application to the Secretary, will be held as follows:—

April 18: Mr. D. W. CUTLER (Rothamsted Experimental Station), *The Protozoa of the Soil.*

May 16: Mr. LEONARD TAVERNER, A.R.S.M., *The Principles and Application of Technical Metallurgical Microscopy.*

Mr. W. M. AMES, M.A., B.Sc., A.I.C., *Applications of the Microscope in the Manufacture of Rubber.*

May 30: Mr. H. B. MILNER, *The Microscopical Investigation of Sands for various Industrial Purposes.*

Enquiry Bureau.

Enquiries have been already received relating to the following matters, and any information relating to them will be greatly appreciated:—

Examination of metals for making machinery.

Examination of crystal structure of fats.

Examination of powders of the same refractive index as Canada Balsam.

Examination of silk used in fine sieves.

How can thin oil deposits be examined with transmitted light in order to determine shape, distribution and thickness?

\* How can one ascertain by means of the microscope the suitability of moulding

sand for producing fine surfaces on castings?

Wanted, a suitable method of cutting sections of soap, and a suitable mounting medium for the same.

What is the best method of testing mounting media for refractive index by means of the Microscope?

\* This subject will be dealt with at the meeting on May 30.

### MINERALOGICAL SOCIETY.

MARCH 13, 1923.

*Dr. A. Hutchison, President, in the Chair.*

**DR. A. HUTCHISON.** *A Graphical Method of correcting Specific Gravity Determinations.*

A diagram was given by which the correction for air displacement and reduction to 4° C. can be read off directly.

**A. BRAMMALL and H. F. HARWOOD.** *The Dartmoor Granite (Widcombe Area).*

Field evidence and analyses support the conclusion that the granite is a composite laccolite, and that four successive stages of intrusion are recorded by (1) dark and relatively basic granites scantily exposed and by certain cognate xenoliths resembling basic segregations; (2) a more acid granite which caps many tors and yields mineral evidence of having assimilated country rock; (3) a still more acid granite intrusion into the latter; (4) minor acid intrusions, felspars, garnet, cordierite, etc., were described, and evidence for differentiation was given.

**C. E. TILLEY.** *Genesis of Rhombic Pyroxene in Thermal Metamorphism; Mineral Associations and the Phase Rule.*

Free-silica hypersthene-bearing hornfels of sedimentary origin can be divided into a calcic and non-calcic group, and considered as derived from a normal shale hornfels by increments either of CaO, (MgO + FeO), or less commonly K<sub>2</sub>O. Silica-poor hypersthene hornfels can be derived from the free-silica types and the hypersthene is then frequently accompanied by spinel. The derivation of all these hornfels can be graphically expressed in systems of three or four components. The hypersthene is derived from the chlorite in the original sedimentary rocks subjected to metamorphism. Hypersthene arises when enstatite, augite, or amphibole-bearing ig-

neous rocks enter contact aureoles, and examples of these are given. Reference is made to the production of rhombic pyroxene by contamination of gabbroic rocks. The hornfels are considered from the standpoint of the phase rule, a classification considered, and the condition of equilibrium in the inner zone of hornfels in contact aureoles discussed.

**C. S. GARNETT.** *On a peculiar chlorite-rock at Ible, Derbyshire.*

A band in the dolerite still at Ible is completely altered to a foliated mass of chlorite, with associated veins of fibrous chlorite (resembling chrysotile in appearance). The analyses and characters of this material are compared with those of "epichlorite."

**C. S. GARNETT.** *The Dissociation of Dolomite.*

The statement in the text-books that dolomite dissociates in two stages, giving when half-burnt a mixture of calcium carbonate and magnesia, is not confirmed. Dissociation is inappreciable up to 625°, and at 898° it is complete. The temperature-dissociation curve is continuous.

**J. G. C. LEECH.** *Occurrences of Rutile, Brookite, and Anatase in the St. Austell Granite.*

These minerals occur in the red pneumatolysed granites of the area, the mode of occurrence being essentially the same as that recorded for Dartmoor occurrences of those minerals.

### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

The next meeting of the Society will be held on Wednesday, April 4, at the Chemical Society's Rooms, Burlington House, Piccadilly, W., at 8 p.m. The following papers will be read:—

*Physiological Standardisation*, by **DR. STANLEY WHITE.**

*An Investigation into the Chemistry of the Reinsch Test for Arsenic and Antimony, and its extension to Bismuth*, by **B. S. EVANS, M.B.E., M.C., B.Sc., F.I.C.**

*The Estimation of Boric Acid in "Liquid Eggs" and other Foodstuffs*, by **G. W. MONIER-WILLIAMS, M.A., Ph.D., F.I.C.**

### THE INSTITUTION OF ELECTRICAL ENGINEERS.

The programme for the summer meeting at North-Western Centre, 5—8 June, will be as follows:—

## Visits.

## TUESDAY, JUNE 5.

Morning (a) The electrically driven rolling mill equipment of Messrs. R. Johnson and Nephew, Ltd., Bradford, Manchester, and the engineering works of Messrs. Mather and Platt, Ltd., Newton Heath; or (b) The No. 2 Dunlop Rubber Cotton Mills, Ltd., Rochdale.

Lunch at the Manchester Town Hall as the guests of the Corporation Electricity and Tramways Committees.

Afternoon (c) Messrs. Pilkington Tile & Pottery Co., Ltd. (makers of the Lancastrian art pottery); (d) The Chloride Electrical Storage Co., Ltd.; (e) The London, Midland and Scottish Railway Company's power station, and, at Ringley, (f) The Lancashire Electric Power Company's station.

## WEDNESDAY, JUNE 6.

Morning.—Proceed at the invitation of the Manchester Ship Canal Co., Ltd., by special steamer from Pomona Docks, viewing the swing bridges and other engineering features en route, to Barton, where the party will disembark and inspect the Manchester Corporation's new generating station.

Lunch at Trafford Park as the guests of the Metropolitan-Vickers Electrical Co., Ltd.

Afternoon.—Visit the works of the Metropolitan-Vickers Electrical Co., Ltd., and the Lancashire Dynamo and Motor Co., Ltd., Trafford Park.

As alternatives to the foregoing visits, members may visit the following places at any time on Tuesday or Wednesday:

(1) The outdoor 33,000-volts sub-station (in High Street) of the Manchester Corporation; and

(2) The *Manchester Guardian* Offices, for the Murray Multiplex System of Telegraphy, and Rotary Printing Presses.

(3) *On Wednesday morning only*, the Laboratories of The University, Manchester, will be open for inspection.

## THURSDAY, JUNE 7.

Alternative morning visits:—

(a) The British Insulated and Helsby Cable Works, Prescott.

(b) (1) The Liverpool Corporation Tramways, Lambeth Road Works.

(2) Automatic Sub-station, Walton.

(3) Lister Drive Power Station.

(c) The Cunard Company's s.s. *Scythia*, or some other big liner.

Alternative afternoon visits:—

(d) Messrs. Lever Bros., Port Sunlight.

(e) The University Applied Electricity Laboratories, where demonstrations in radio reception will be given, and The Automatic Telephone Manufacturing Co., Ltd.

(f) (If sufficient applicants):

(1) The Liverpool Corporation Tramways, Lambeth Road Works.

(2) Automatic Sub-station, Walton.

(3) Lister Drive Power Station.

Note—As other alternatives to the afternoon visits, members may also visit: (g) The Mersey Power Co., Runcorn (the company will arrange for tea and transport at Runcorn); (h) The United Alkali Company's Power Station, Widnes; (i) The London, Midland and Scottish Railway, Southport Electrified Line.

## FRIDAY, JUNE 8.

Morning.—Leave Liverpool by special train for Llandudno Junction, where the party will transfer to motor coaches and proceed by alternative routes as follows:—

(a) Via Conway Valley, Bettws-y-Coed, Capel Curig, Llanberis or Nant Ffroncon Pass to Carnarvon and Bangor, returning along the coast road to Llandudno; a halt will be made at Dolgarrog to inspect the hydro-electric power station and works of the Aluminium Corporation, Ltd.

(b) Generally as (a) above, but the halt will be made at Pen-y-Gwryd to inspect the North Wales Power Company's hydro-electric station at Cwm Dyli.

(c) Generally as (a) above, but the halt will be made at Lord Penrhyn's Slate Quarries, Bethesda.

A meeting was held on Thursday, March 22, when a discussion on papers by MR. FRANCIS HOOPER and MR. J. W. BEAUCHAMP, on the *Co-operation between the Architect and the Electrical Engineer*, was continued.

The January issue of the *Journal of the Chemical Society of Japan* contains the following papers communicated to the Society.

*The Detection and Separation of Iridium*, by ISABURO WADA and LUNAO ATO.

*Uses of Alloys in Volumetric Analyses, Part VIII. On the Determination of Chromium and of Iron Accom-*

*panying with Chromium*, by NAOTSUNA KANO.

*Uses of Amalgams in Volumetric Analyses, Part IX. On the Determination of Titanium and of Iron Accompanying with Titanium*, by NAOTSUNA KANO.

*On the Nitrogenous Compounds in the Flesh of *Mactra sulcataria*, Desh*, by KIYOHISA YOSHIMURA.

*On the Nutritive Value of the Proteins of Soy Bean and Pea Nut*, by TOKITAKA SHIBA and MANSHI KOYAMA.

*On the Protein of Rice Embryo and its Nutritive Value*, by MATSUKICHIRO HAMADA.

*Preparation of Petroleum from Fatty Oils, Part II.*, by MASAKAZU INONYE.

### CORRESPONDENCE.

#### THE TITLE, "CHEMIST."

To the Editor of THE CHEMICAL NEWS.

SIR,—The Retail Pharmacists' Union, in their recent announcement with regard to the subject of the accurate dispensing of medicines have, I think it will be generally agreed, made a good statement on behalf of the profession of pharmacy.

I would, however, venture to place before your readers a matter, arising from the above, which is one of no small concern to those chemists who are engaged in the practice of *Chemistry* as distinct from *Pharmacy*—that is to say, who are concerned with the science of chemistry and its applications to the arts and manufactures, and have nothing to do with the dispensing of medicines.

The Retail Pharmacists' Union have headed their announcement with the words "*The Chemist*," and I would like to make, in the public Press, the suggestion which has so often been made in the scientific Press, that the time has come for the pharmacist to relinquish the use of the term "chemist" in favour of those who definitely practise chemistry.

The war was instrumental in directing the attention of the public more closely to the existence of the profession of chemistry, the profession on which the country found it necessary to rely for the production of explosives and materials of war generally, as well as for the means of protecting our troops against the methods of chemical warfare initiated by the enemy.

During the past half-century, the science of chemistry has developed by leaps and bounds, and its practice as a profession has become more and more firmly established. In this country the science is now taught in 1,000 or more public and secondary schools, and in nearly 300 technical schools, while our University Departments of Chemistry are renowned throughout the world.

The Institute of Chemistry, as the representative Chartered professional body of chemists, numbers upwards of 4,000 Fellows and Associates, whose qualification demands a four years' University course, or the equivalent, and the majority of whom are engaged in the many branches of industry on which the science has a bearing.

In other countries, the strict equivalent of the word "chemist" signifies, as it should, one who professes chemistry, and not in any case the pharmacist, druggist, or dispenser of medicines. How the misapplication of the word has arisen in this country is a matter which I need not here pursue. The enormous importance of chemistry is becoming daily more widely recognised, and it is highly desirable in order to avoid confusion, that the word "Chemist" should be confined to those who practise chemistry in the full sense of the word. It is bad enough when mental confusion is the unfortunate consequence of the poverty of a language, but in this instance the correct and distinctive words are ready to our hand.

I would like to express the hope which I have already expressed on a good many occasions, that our friends the Pharmacists—notwithstanding the provision of the Pharmacy Act—will lose no opportunity of referring to their ancient and important calling by the word which more accurately defines and describes it. In addition, I would appeal to the Press, which is so important a factor in the enlightenment of the general public, to assist so far as they can by employing the terms "Chemist" and "Pharmacist" respectively in their obviously correct significations, so that those practising chemistry may be described as Chemists, and those practising pharmacy as Pharmacists.—Yours, &c.,

A. CHASTON CHAPMAN, F.R.S.,  
President of the Institute of Chemistry  
of Great Britain and Ireland.  
30, Russell Square, London, W.C.  
March 17, 1923.

## NOTICES OF BOOKS.

*The Chemist's Year Book*, 1923. Edited by F. W. ATACK, M.Sc. (TECH.), D.Sc., F.I.C., assisted by L. WHINYATES, A.M.C.T., A.I.C. In two volumes. Pp. VII. + 1,108. Manchester: Sherratt & Hughes, 34, Cross Street. 1923. 21s. 9d., post free (abroad 22s.).

English-speaking chemists have for several years had the opportunity of possessing a volume (or rather two) convenient for the pocket and containing an enormous amount of information such as is frequently needed in the ordinary course of their work. That this is the 8th edition is sufficient testimony to indicate how much the *Chemist's Year Book* is appreciated.

In this edition a new section on Leather Analysis, by W. Mather, A.M.S.T., A.I.C., has been incorporated. Various sections have been revised and corrected where necessary, in accordance with the results of the most recent researches.

*The Chemist's Year Book* for 1923 should thus prove as popular among chemists as its predecessors have been.

J.G.F.D.

*Vat Colours*, by JOCELYN FIELD THORPE, D.Sc., Ph.D., F.I.C., F.R.S., and CHRISTOPHER KELK INGOLD, D.Sc. Pp. XV. + 491. London: Longmans, Green & Co., 39, Paternoster Row, E.C.4. 1923. 16s. net.

It has long been recognised that fast colours can only be imparted to fabrics by forming the coloured compound within the fibres of the material to be dyed.

The vat dyes include chemically very dissimilar types such as indigo, indanthrene and indophenol. The essential feature is that the substance must possess a carbonyl group, capable of being reduced to the group  $C \cdot OH$ , forming a leuco-compound, soluble in alkalis.

The vat colours are usually insoluble in ordinary solvents, and are applied in the form of colourless and soluble reduction products.

Re-oxidation by exposure to air develops the original colour within the fibre.

Of the vat dyes, the "Purple of the Ancients," and especially Indigo, were known to the earliest dyers, and the authors have rightly devoted adequate and careful attention to the history of these

colours. Indigo was, until the last few decades, the only vat dye of commercial importance.

Baeyer's extensive researches, and also those of other German chemists which led to the elucidation of its structure, were followed by various syntheses of indigo itself, and subsequently by the preparation of similar dyestuffs of different shades.

These syntheses also revealed the essential structure of the vat dyes, and more recently, important new types of these compounds have been produced from anthraquinone. The authors give a complete account of these bodies, some of which are very complex, and whose molecules contain many condensed rings.

The last section of this very complete monograph gives detailed instructions for the preparation of the dyes themselves, and also their intermediate products.

An appendix gives a list of British vat dyes and their German equivalents.

The monograph will be of great service to chemists and others engaged in the dye industry, since it is the only volume dealing exclusively and comprehensively with this class of dyes. It will also be widely consulted by the general scientific world

*Back to Prosperity*, by HENRY LOWENFELD and his daughter, MARGARET-LOWENFELD. Pp. 268 + XII. London: Effingham Wilson, 16, Copthall Avenue, E.C.2. 1923. 5s.

This very original volume on the intricacies of monetary systems and present anomalies arising from the chaotic state of foreign exchanges, should prove of interest and importance to those connected with the financial side of chemical and other businesses.

## BOOKS RECEIVED.

*Atoms*, by JEAN PERRIN, translated by D. H. HAMMICK, M.A. Pp. XIV. + 231. Second English Edition. 1923. Messrs. Constable & Co., Ltd., 10 & 12, Orange St., Leicester Square, W.C.2. 8s. 6d. net.

*Readable School Chemistry: A Book for Beginners*, by J. A. COCHRANE, B.Sc. Pp. IX. + 84. 1923. Messrs. G. Bell & Sons,

Ltd., York House, Portugal Street, W.C.2.  
2s.

*The Generation and Utilisation of Cold: A General Discussion*, by THE FARADAY SOCIETY. Pp. 137, 141 + 273. 1923. The Faraday Society, 10, Essex Street, Strand, W.C.2. 10s. 6d. net.

*A Tested Method of Laboratory Organisation*, by SEYMORE PILE, M.A., and REGINALD G. JOHNSTON, with an Introduction by W. R. BARCLAY, O.B.E. Pp. IX. + 98. 1923. Messrs. H. F. & G. Witherby, 326, High Holborn, W.C. 7s. 6d. net.

*The Destructive Distillation of Wood*, by H. M. BUNBURY, M.Sc. (Bris.), B.Sc. (Lond.). Pp. XIX. + 328. 1923. Messrs. Benn Brothers, Ltd., 8, Bouverie Street, E.C.4. 35s. net.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 5699—Amber Size & Chemical Co., Ltd.—Production of aluminium hydroxide and alkali silicates. Feb. 27.
- 5716—Asheroff, E. A.—Apparatus for electrolyzing fused salts of metals and recovering metals and acid radicles. Feb. 27.
- 5576—Boudett, A. E. P.—Reduction of calcium sulphate. Feb. 26.
- 5856—Coley, H. E.—Extraction of gold from arsenical ores. Feb. 28.
- 5894—Dutt, E. E.—Preparation of manganese dioxide. March 1.
- 5746—Harnist, C.—Manufacture of fertilisers from sulphur. Feb. 27.

- 6015—Pinel, A.—Ripening alkali cellulose for manufacture of cellulose xanthate. March 1.
- 6016—Poma, G.—Manufacture of p-amino-phenol. March 1.
- 5877—Royston, G.—Drying sulphate of ammonia. March 1.
- 5877—Saville, W.—Drying sulphate of ammonia. Feb. 28.
- 6235—Standard Development Co.—Dehydrating alcohol. March 3.

#### Specifications Published this Week.

- 193071—Plauson's Parent Co., Ltd. (Plauson, Dr. H.)—Process of producing lower boiling hydrocarbons from high-boiling hydrocarbons.
- 176779—Norsk Hydro-Elektrisk Kvaestof-aktieselskab.—Process for the manufacture of hydrogen, carbonic oxide or mixtures of these gases.
- 193304—Quinan, K. B.—Manufacture of superphosphate.
- 193477—O'Shaugnessy, F. R.—Method of and apparatus for the de-colloiding of colloidal organic matter, and the destruction of the offensive character of putrescible organic matter.
- 193551—Chemische Fabrik auf Actien (vorm E. Svhering).—Process for solidifying formic aldehyde.
- 193618—British Dyestuffs Corporation, Ltd., and Perkin, W. H., and Clemo, G. R.—Manufacture of a new chloroethyl-ester and the treatment of phenols, alcohols, and amino-compounds therewith.
- 193789—Casale, Dr. L., and Leprestre, R.—Apparatus for the catalytic synthesis of ammonia.

#### Abstract Published this Week.

- 191687—Ferrocyanides.—Silver Springs Bleaching and Dyeing Co., Ltd., and Hall, A. J., Timberbrook, Congleton, Cheshire.

The waste liquor from aniline black dyeing in which ferrocyanide is used, is treated with ferrous sulphate so as to obtain a blue precipitate as described in the parent case, and the blue precipitate is separated and dissolved by means of an alkali, alkaline earth, or ammonia. The iron hydrate also produced is separated from the solution and the ferrocyanide is obtained by crystallisation from the filtrate.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3286.

## THE STYLE OF SCIENTIFIC LITERATURE.

"What one fool can do, another can."

This sweeping assertion is to be found on one of the fly-pages of the late Professor Silvanus P. Thompson's book, *Calculus Made Easy*. The assertion is rather significant, and we should hesitate to contradict it, but a great moral lies in the words.

At the time when Professor Thompson wrote the book in question, he probably held pronounced views upon how Science should be regarded, and gives one the impression that he looked upon it as a huge joke, not to be inconsiderately thrust aside, but to give food for deep reflection.

Whatever may be the attitude of the student of Science to his subject, the writing of a scientific book is, essentially, a teaching process, whether it be an elementary text-book or an exposition upon some greatly obscure discovery. Yet how often has a chemist sat down in the evening with a pile of laboratory results before him, almost groaning with vexation because the works of reference he must of necessity use are tedious and prolix? They contain the information he requires, but he is only able to find it by much wading through a hideous sequence of almost incomprehensible words. Incoherency of text often worries him still more.

One can learn more in ten minutes from a book of the type Professor Thompson has written than from three hundred pages of unrelieved letterpress in several hours, and this is not an hyperbolic assertion by any means. One is interesting in itself; the other is not, but only in the matter it contains. We do not maintain that every book of scientific tendencies should be compiled similarly, for it would be an impossible expectation; but if the compilation was less elaborate, it would save the research chemist much valuable time. The exact difference is in writing what one may have to write within 200 pp. of large, widely-spaced print, and putting down precisely the same information in double the page-quantity of small print.

The matter has been discussed widely before now. Present conditions make fresh

comments desirable. Formerly, admission to the learned professions was made only via the Universities; now, it is purely a question of initiative on the part of those who have not the means of studying at the higher educational centres. They must gain their knowledge mainly from books, and simplification is, to them, desirable.

## VALENCY.

BY WILLIAM R. FIELDING, M.A., M.Sc.  
(VICT.).

Senior Science Master, King Edward VII.  
School, Lytham.

(Continued from Page 197.)

All these compounds are exothermic, i.e., as the energy of the system is reduced,  $p$  is increased, and we may safely predict that as heat is absorbed  $p$  is reduced.

When an exothermic compound is heated  $p$  is reduced; as a substance is cooled  $p$  is increased — again showing that as the energy of a system is increased  $p$  is reduced whereas as heat is taken out of a system the substance, either element or compound, becomes more polymerised. The maximum of polymerisation occurs at the absolute zero (see *The Chemical News*, Vol. CXXIII p. 97).

The halide acids illustrate this well, for the gaseous state.

	Heat of formation.
HF	+ 38,500 cal.
HCl	+ 22,000
HBr	+ 8,440
HI	- 6,040

Hydrofluoric acid is undoubtedly polymerised at 300° A. ( $H_xF_x$ ) and is  $H_xF_x$  (where  $x > 2$ ) at still lower temperatures. On the other hand, HI is endothermic, and it is not only less disposed to polymerise, but it is readily decomposed into its constituents. There is a kind of law of direct self-preservation—the more energy leaving the system and the more organised ( $p$ ) does the system become. There seems grounds for believing that the different valency-values obtained by the different methods may be due in part to ignoring these charges in the energy of the system.

It is this variable quantity of energy which appears as heat-energy one moment and polymerisation another which accounts

for the many inexplicable exceptions to our preconceived valency-values.

	Latent Heat. p.	Heat absorbed.
Ice ....	80	3
Water . .		<2
Steam . .	537	1

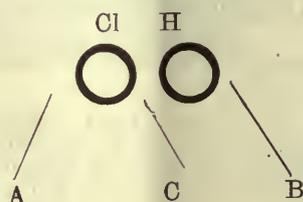
↓

Data respecting endothermic compounds are not very abundant, but for

	T	p
CS <sub>2</sub> (Liquid) .....	243	1.88
	273	1.88
	303	1.93

(see *The Chemical News*, CXXII., 289).

An atom of hydrogen consists of a positive nucleus and one (negative) electron. As the temperature is raised the tendency to polymerise with other hydrogen atoms is reduced; so is the density; therefore the atomic volume is increased. This may be due to the electron increasing its distance from the + nucleus. If in combination with a chlorine atom, the hydrogen atom will tend to be electro-negative on the chlorine side and electro-positive on the side remote from the chlorine. If the electron enters the chlorine atom, or if it is only supposed to come to the "point of contact" or be the "point of contact" of the two atoms, there will be a readjustment of the electrical forces within the two atoms (Fig. XX.):



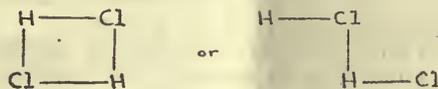
(Fig. 20.)

A.—Owing to the acceptance of electron from hydrogen there will be a disturbance in the orbits of at least some of the electrons of the chlorine atom. This side of the chlorine becomes electro-negative.

B.—This side becomes electro-positive.

C.—The electron accepted by the chlorine from the hydrogen.

Hydrochloric acid may become polymerised thus:—



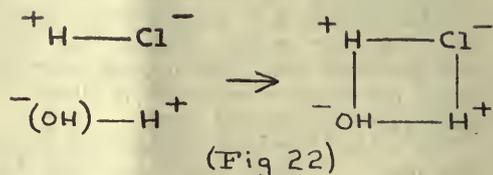
(Fig. 21)

From the study of radio-active substances it is accepted that existing atoms have a positive nucleus and negative electrons. Are there, or have there been, any atoms with a negative nucleus and positive electrons?

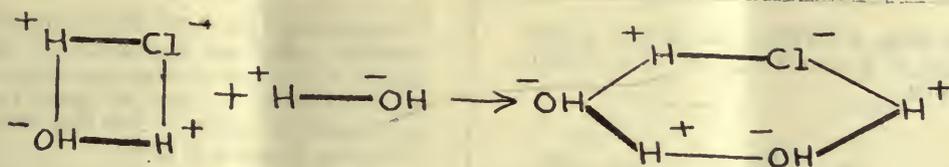
Such a supposition would readily account for all combinations, except possibly in the case of the amphoteric elements. Consider the union of hydrogen and chlorine, an electro-positive nucleus in the former case and an electro-negative nucleus in the latter. Union is caused by a + electron from the chlorine neutralising an electron of the opposite sign from the hydrogen. (On separating the two atoms, the equal and oppositely charged electrons are restored to their original positions in the respective atoms.) The hydrogen part of the hydrochloric acid molecule would be electro +, and as in the former case may be able to effect combination with an electro-negative element other than the chlorine with which it is already combined. Through the loss of one of its + electrons the chlorine is electro-negative and likewise may be able to effect combination with an electro + atom or radicle. Even the amphoteric elements need not offer serious trouble. We have to account for the combination of two electro-positive atoms in the molecule in H<sub>2</sub>, and of two electro-negative atoms in Cl<sub>2</sub>. In such cases the union may be effected by the + nucleus in one atom attracting the electron in the other atom thus:



Hydrochloric acid forms several well-defined hydrates, e.g., HCl.H<sub>2</sub>O and HCl.2H<sub>2</sub>O. How do the acid and water combine? The signs opposite the symbols indicate whether the atom is electro-positive or negative. It is presumed, for the reasons given above, that combination with an atom or group of opposite sign may, in certain circumstances be effected (Figs. XXII. and XXIII.):



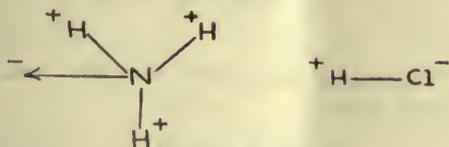
(Fig. 22)



(Fig 23)

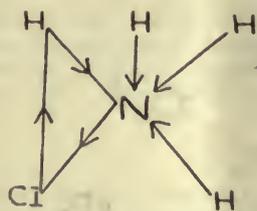
The thickened lines in Fig. XXIII. show the position of the main, principal or dominant valency.

Ammonium chloride may be derived in the same way from ammonia and hydrochloric acid, as in Fig. XXIV.:



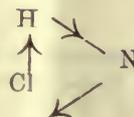
(Fig 24)

Nitrogen is slightly more than trivalent towards hydrogen, possibly not tetravalent, but the hydrogen and chlorine of the hydrochloric acid, approaching it at the same time, make it appear to be pentavalent, the chlorine partially returning the electron it has received from the hydrogen, which now becomes slightly electro-positive towards the nitrogen which is now in a position to transfer (partially) an electron to the chlorine. The return of the electron from the chlorine to the hydrogen, and from the hydrogen to the nitrogen, and lastly from nitrogen to the chlorine, may not be completed but by readjustments in their electronic orbits these three elements are in equilibrium. Ammonium chloride would be represented as in Fig. XXV., the arrows showing the direction in which the electrons tend to be transferred.

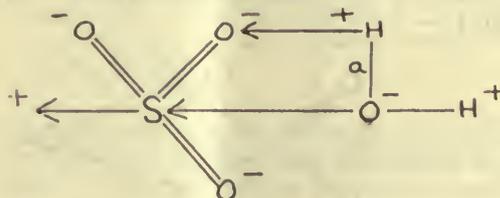


(Fig 25)

Unlike many rings, the ring

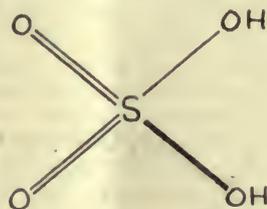


is easily ionisable in the presence of water. Sulphuric Acid.—Here sulphur is electro-positive to oxygen (Fig. XXVI.):



(Fig 26)

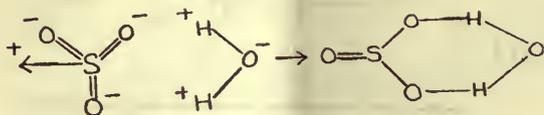
The water combines with the SO<sub>3</sub>, one hydrogen joining on to an oxygen and the oxygen in the water directly linking with the central atom, sulphur. There is then a redistribution of valency as there are now four atoms or groups joined to the sulphur, with the result that valency *a* disappears. This is an exothermic action, and part of the heat evolved may be due to the rearrangement of the valencies.



(Fig 27)

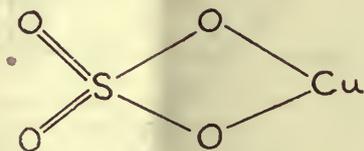
Fig. XXVII. shows the dibasic nature of the acid, whereas an alternative method of

linkages (Fig. XXVIII.) would lead to the formation of a closed ring which are often unionisable.



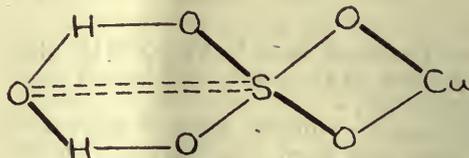
(Fig 28)

Fig. 28 may represent a temporary isomeric form which passes into the compound represented by Fig. 27 by the oxygen atom at the extreme right joining on to the sulphur. The former arrangement is to be preferred, not only because the valencies are the usual valencies of these elements, but because it shows the formation of the sulphates in a more straightforward way, thus:—



(Fig 29)

Sulphuric acid and the sulphates form hydrates, and the first molecule of water seems to occupy a unique position, and is more difficult to drive off than the other molecules of water. For this reason the following formula is given:



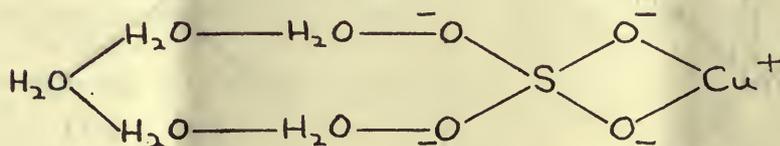
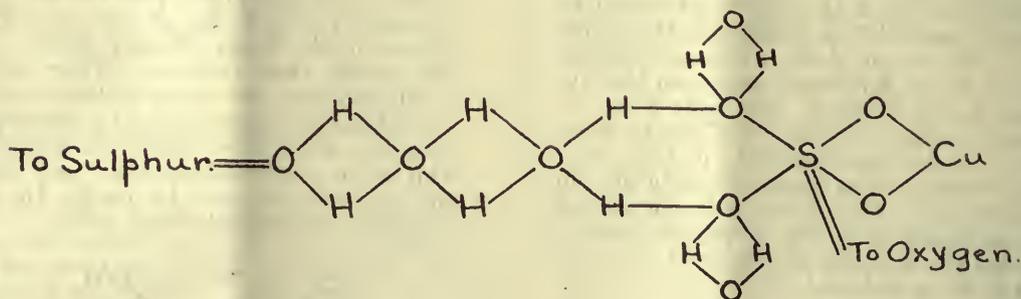
(Fig 30)

Four other molecules of water can be added, thus:

(See Fig. 31.)

Many rings are non-ionisable, but a solution of copper sulphate is readily precipitated by a solution of  $\text{BaCl}_2$ ; evidently the above rings are very unstable in aqueous solution.

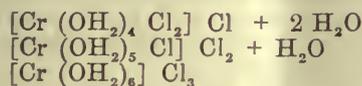
A few examples of non-ionisable rings will now be given.



etc.

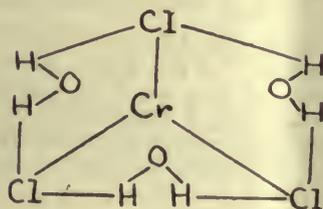
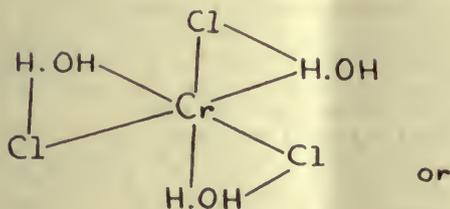
(Fig 31)

*Chromium trichloride.* — Three crystalline hydrates are known,  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ , two green and one violet. Werner represented these as follows:



The chlorine outside the square brackets is ionic.

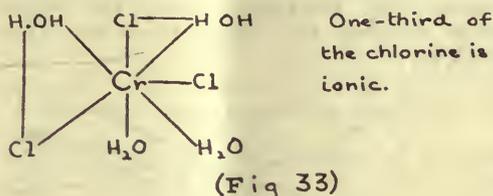
I prefer to think that the anhydrous chloride combines with three molecules of water and forms three closed rings, thus:



(Fig 32)

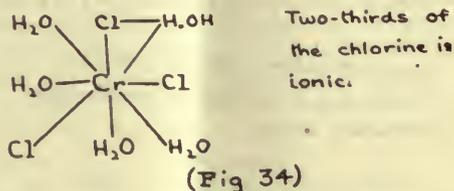
None of the chlorine is ionic. The chromium appears to be hexad. Considering one ring (1st formula), the chlorine receives an electron from the chromium, and with it it compensates the hydrogen to which it is directly attached, and enables it to hold the OH group and also to link up the chromium.

If another molecule of water is added to the molecule it breaks up the first ring and the chlorine which is freed becomes ionic (Fig. XXXIII.):

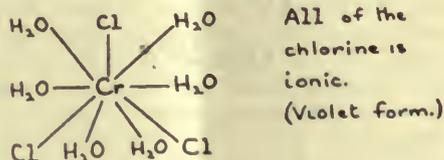


(Fig 33)

The second and third rings are broken up by successive molecules of water:



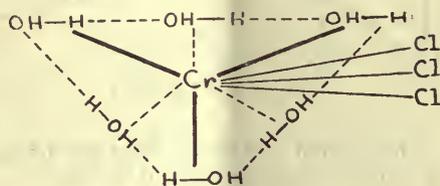
(Fig 34)



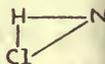
An alternative method would be to link the water and chlorine as in the second formula. The final form is the same in each case.

Thus chromium is attached by principal and subsidiary valencies to 6, 7, 8, or 9 atoms or groups. Six of these are water molecules in the last case and undoubtedly these water molecules will exercise valency towards each other to form polymers similar to di- and tri-hydrol in liquid and solid water. In any cases the valencies usually given to chromium cannot hold, because if these six molecules had a single resultant residual valency towards the nuclear chromium atom the valency of the latter would be 4. To mark the valencies between the chromium and the chlorine and to ignore the molecules which are included in the complex ion is simply shelving the matter. The heat change accompanying every chemical and physical change effects a change in the energy of the system, and the valency of any and every atom will be altered in some degree. There is no valid argument against hydrogen becoming dyad or triad and oxygen pentad. The weight carried by a person depends, to some extent, on the distribution of the load. The following seems to be the simplest way of

representing the complex ion, the dotted lines showing the weak valencies (Fig. XXXV.):



Thus the  $\begin{array}{c} \text{Cl} \\ | \\ \text{Cr} \end{array}$ —H.OH ring is non-ionisable, whereas the unstable ring present in ammonium chloride is:-



(Fig 35) •

(To be continued.)

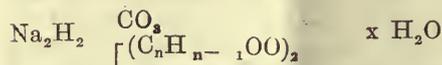
## COMPOUNDS OF SODIUM CARBONATE WITH FATTY ACIDS.

By J. F. WEINBERG.

[*Editorial Note.* — This communication was sent under seal to the late Sir William Crookes, F.R.S., on December 26, 1919. Recently, efforts to get into touch with the author have failed. The seals were thereupon broken, and the article is now published.]

### PREPARATION.

Fatty acids in a melted state readily combine with crystallised sodium carbonate (10 ag.) when melted in its water of crystallisation. A series of compounds is formed of a chemical character, much resembling sodium bicarbonate, its composition being represented by the formula:



### PROPERTIES.

These compounds can with great advantage be used instead of soap.

The effect on the skin is milder, no caustic soda being present or set free by hydrolysis.

The effect during ablutions is very remarkable.

The exudation from the human skin is a solution of organic nitrogen compounds in volatile fatty acids.

In foul linen these volatile fatty acids are soon evaporated, leaving a residue insoluble in caustic soda and insoluble in soap.

Therefore, soap will never make foul linen clean, scrubbing and bleaching agents being indispensable.

However, this residue is easily soluble in a hot aqueous solution of the above-mentioned compounds. It is also soluble in hot dilute hydrochloric acid (0.1 per cent.), which seems to account for the action of chlorine in the presence of moisture.

Boiling for half an hour in a 1-2 per cent. aqueous solution of the compounds just described, will clean the foulest linen, mechanical treatment, as well as bleaching agents being altogether superfluous.

### PREPARATION ON A LARGE SCALE.

The fat to be used is saponified, then decomposed by sulphuric or hydrochloric acid. Any other process may likewise be used to obtain the fatty acids.

The fatty acids are simply melted, and in this state added to sodium carbonate (10 H<sub>2</sub>O) melted in its water of crystallisation.

When the mixture is stirred, the reaction is complete. No carbonic acid is set free, all of the water of crystallisation may remain in the product.

Fatty acids prepared from Sunlight soap (the melting-point of the acids was 27° C.) give a product of very much the same appearance, only being a little harder.

The proper proportions are approximately: 1 part of fatty acids to  $\frac{1}{2}$  part of carbonate of soda (10 H<sub>2</sub>O). However, an excess of carbonate of soda seems advisable. Good results were obtained with: 1 part of carbonate of soda, 1 part of fatty acids.

## CONCENTRATED BORATE OF LIME.

By E. L. FLEMING.

Crude borate of lime contains 28.2 per cent. anhydrous boracic acid. Its value delivered, at 7s. 3d. per unit, is £10 5s. per ton, which does not pay cost of collection and transport. If it is dried and contains 43 per cent. A.B.A. its value delivered is £15 13s. per ton.

By removing 63 per cent. of the worthless material associated with the borate of lime, freshly drawn from the deposit, a concentrated borate is produced containing

75 per cent. A.B.A., and its value delivered is £27 6s. per ton. The process is quite simple, the materials used for its production being products of the countries where the borate of lime is located. The approximate cost of production at the Boratera, for one ton of concentrated borate, working with the smallest plant, with an output of 300 tons per ann. being £12 per ton. It may be worked with unskilled native labour. The plant for producing concentrated borate can be obtained from a well-known firm of chemical engineers in England.

The advantages possessed by concentrated borate 75 per cent. A.B.A. are that by boiling it with half its weight of 58 per cent. alkali, it produces 200 per cent. of its weight in crystal borax. The solid refuse only amounts to 7 per cent. There is a saving of 42 per cent. in transport, when compared with calcined borate 44 per cent. anhydrous boracic acid.

In Argentina, borate of lime ground covering an area of 76,000 hectares has been recorded in the State Mining Roll. The level at which these borateras are located is reached by the Central Northern Railway, at Tres Cruces. In Bolivia, by the Arica-la Paz Railway at Charana. In Chile, by the Antofagasta and Bolivian Railway at Ascotan. In Peru, by the Arequipa Railway at Pampa de Arrieros.

The borate of lime occurs in three distinct formations:

- (1) In layers on the surface of the ground.
- (2) In banks, five or six feet in depth.
- (3) In the form of "potatoes" or rounded masses, scattered throughout the soil.

### ACTIVE HYDROGEN: NEW METHODS OF PREPARATION.

By Y. VENKATRAMAIAH.

Continuing his researches on the activation of hydrogen, the author has elaborated four more new methods of activating the gas. The new methods are:

(a) The burning of oxygen in hydrogen.—The hydrogen and oxygen utilised in all the experiments conducted was prepared by electrolysing a solution of barium hydroxide. The gases were purified and dried in the usual way.

The combustion of oxygen and hydrogen was carried out in a specially constructed apparatus kept cool at 0° C. The combus-

tion tube was of platinum, of 12 mm. internal diameter. The oxygen flame was nearly six inches in height. The unburnt hydrogen was drawn out through a tube kept in iced water, on to cold powdered sulphur, and the presence of hydrogen sulphide was tested by using a lead acetate paper.

(b) The surface combustion of hydrogen and oxygen on platinum.—In this experiment a platinum wire 3 metres in length and 0.4 mm. in diameter was wound round a glass rod frame 10 cm. in breadth and 12 cm. in length. The wire was electrically heated by placing the frame in a suitable apparatus into which a proper mixture of oxygen and hydrogen could be introduced containing slight excess of the latter. The presence of activated hydrogen in the uncombined gas was recognised in the usual way.

(c) High tension arc in hydrogen.—A high tension arc was established between two silver electrodes 5 mm. in diameter. The electrodes were kept 1½ cm. apart. A large induction coil whose primary could be fed with a current up to 20 amperes was used along with a Wehnelt interrupter. The presence of active hydrogen in the gas drawn out was tested in the usual manner.

(d) High temperature arc in hydrogen.—In this case hydrogen was conducted into arcs established between metallic electrodes 1 cm. in diameter, of gold, platinum, and silver fixed in a suitable apparatus. The electrodes were kept fed with a current of 6 amperes under 220 volts pressure. The presence of the active gas in the hydrogen drawn out from the arcs was tested as previously described. In the case of silver, activation of hydrogen was possible, while in the case of gold and platinum it was not. An explanation for this discrepancy seems to be in the absorption of active hydrogen by thin films of metals in the case of gold and platinum which are known to absorb larger quantities of hydrogen than silver itself.—(From the *Proceedings of the Science Association*, Maharajah's College, Vizianagram, Dec., 1922.)

### COMPRESSIBILITY, INTERNAL PRESSURE, AND ATOMIC MAGNITUDES.

By THEODORE W. RICHARDS.

The contraction of elements in the formation of compounds has been evaluated

from the determined compressibilities of the individual elements.

In the pressure-volume curves for sodium and potassium, which extend over a range of 45,000 atmospheres, considerable identity with Bridgeman's values (*Proc. Am. Acad. Arts Sci.*, 1922, LVIII.) is disclosed, and the assumption that they are more or less accurate is justifiable. The extant irregularities are considered due to the volume, rather than the pressure or the two together, and the ultimate pressure is computed as the sum of internal and external, giving an equation of the type:  $(p+P)fv = K$ ; where  $p$  = the external, and  $P$  = the initial internal pressure. A close study into the curves revealed a formula notable for its simplicity:  $(V-B)(p+P) = K$ . According to this, the  $B$  portion acts as if it were incompressible, and "the action of the total pressure (external plus internal) to volume is simply hyperbolic. Tabulation of the  $K$ -volumes shows similarity between the calculated and observed values of  $V$ .

The curve seems to have bearing upon the contraction which occurs when potassium and chlorine combine to form potassium chloride. The sum of the gram-atoms of these elements is 70.5 cc., and the reduction takes place over a range of 33.0 cc., the final volume being 37.5 cc. The range of compressibility of chlorine is nearly that of potassium; thus, if potassium at 44,000 atmospheres is reduced to half its original volume, the average  $P$  of potassium chloride is of the same order.

As separate from monatomic molecules, polyatomic molecules demand recognition of the fact that two or more internal pressures must exist; those caused by chemical affinity and those due to material cohesion. The polyatomic curve, then, will be complex; one with a hyperbola similar to that of  $K$ , and the other almost horizontal, corresponding to the greater pressure on certain parts of the atoms. The two curves may be roughly depicted by one hyperbola.

Phosphorus trichloride presents an instance. The behaviour of a millilitre as far as 12,000 atmospheres conforms to the equation  $(p+6200)(V-0.67) = 2050$ ; the large value of  $B$  corresponding to unit initial volume.

There has been no first-hand data computed for chlorine, as the subjection of this element to high pressures is difficult in modern apparatus. Some figures were ob-

tained, however, which admitted of plausible calculations over the chloride range. The contentions are based upon observance of the respective compressibilities of chloroform and carbon tetrachloride, and by comparing chloroform with bromoform (Richards and Stull; *Carnegie Inst. Pub.*; 1903, VII., 44). The comparison rendered the indicative equation:—

$$\beta_{Cl} = \beta_{CHCl_3} \times \frac{\beta_{Br}}{\beta_{CHBr_3}}$$

this conclusion being drawn from the fact that the differences between the boiling points of chlorine and bromine, and the two derivatives mentioned, are approximately identical.

Phosphorus trichloride seems to throw some light upon the problem. The compound contains rather over  $\frac{1}{3}$  of its weight of chlorine, and the phosphorus must obviously be compressed to a smaller bulk than either white or red phosphorus. A study of the two volumes shows that the chlorine is in a similar condition to independent liquid chlorine. From these inferences, a curve depicting the behaviour of liquid chlorine may be obtained; it being confirmed by the compressibilities of both bromine and iodine.

The numerous data comply invariably with observations contained in an earlier communication; but the modified principles clarify to a considerable extent the curious actions of many solids and liquids, and further discussion upon some of them will follow in the near future.

[Substance of a Contribution from the Wilcott Gibbs Memorial Laboratory of Harvard University; quoted from the *Journ. Amer. Chem. Soc.*, 1923, XLV., 422.]

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### ROYAL SOCIETY OF ARTS.

##### INDIAN SECTION.

Friday, April 6th, 1923, at 4 p.m.

Postal and Telegraph Work in India, by

GEOFFREY ROTHE CLARKE, Esq., C.S.I. O.B.E., I.C.S., Director-General of Posts and Telegraphs in India.

The Right Hon. Lord Montagu of Beau-  
lieu, K.C.I.E., C.S.I., will preside.



### SOCIETY OF GLASS TECHNOLOGY.

The President, Prof. W. E. S. Turner, D.Sc., presided at the meeting of the Society of Glass Technology, held in the University, Birmingham, on Wednesday, March 21st, 1923. The papers presented were all contributions from the Department of Glass Technology, The University, Sheffield.

The first one, entitled *A Rapid Method of Testing the Durability of Glassware*, by Mr. H. S. BLACKMORE, Miss VIOLET DIMBLEBY, and Prof. W. E. S. TURNER, was read by Miss V. Dimbleby, who was thus the first lady to read a paper before the Society. The paper presented an account of a simple and rapid method for determining whether a sample of glass would withstand weathering sufficiently to enable it to fulfil certain purposes. The test consisted of the fact that when a very dilute solution of one part in 1,000 of the alkaloid narcotine hydrochloride is heated to boiling inside a glass vessel, the alkaloid is thrown out of solution, and can be seen as a fine precipitate if the glass is of poor quality. If this occurred at the end of ten minutes' heating, the glass was to be condemned; if within twenty minutes, the glass, although better, was still unsatisfactory.

Good glasses ought to show no sign of deposit when heated at the boiling point for an hour. It was pointed out that this test differed from all the others previously devised and used, in that it required no special chemical knowledge, could be carried out with very simple apparatus, and therefore was a test which could be applied in any factory. The test was shown to be thoroughly satisfactory by a large number of trials on all kinds of glassware.

The two other papers contributed were: *The Corrosion of Fireclay Refractory Material by Glass and Glass-making Materials*, by Mr. DONALD TURNER and Prof. W. E. S. TURNER, and *The Effect of Saltcake in Corroding Fireclay Materials*, by Miss EDITH M. FIRTH, Mr. F. W. HODKIN, and Prof. W. E. S. TURNER. These two papers were taken together and presented by Prof. Turner, who detailed experimental evidence showing that in glass melting the corrosion of the pots or of the tank blocks was most severe during the early stages of the melting of the batch. The corrosion due to the glass itself was proved to be very much less.

Of the glass-making materials, sodium nitrate, potassium nitrate, and borax were

particularly corrosive. Resistance to corrosion could be improved by firing the pots or blocks at 1,400° before the charge of batch was inserted. At temperatures round about 800 or 900° C., saltcake was not nearly so corrosive as soda ash. At the temperature of the melting furnace, however, it appeared to be more corrosive, and it was demonstrated by a series of experiments that as the proportion of saltcake increased, so did the extensiveness of corrosion, even in batches in which coke, as a reducing agent or the saltcake, was present throughout.

During the forenoon a party of members visited the Longbridge Works of Messrs. Austin Motor Co., Ltd., Northfield.

### INSTITUTION OF PETROLEUM TECHNOLOGISTS.

#### SEVENTIETH GENERAL MEETING.

At the House of the Royal Society of Arts, John Street, Adelphi, W.C.2.

On Tuesday, 10th April, 1923, the following paper will be read:

*Potrero No. 4. A History of One of Mexico's Earliest and Largest Wells*, by A. E. CHAMBERS, M.Inst.P.T., Assoc.M.-Inst.C.E.

The chair will be taken at 5.30 p.m. by the President, H. Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst. Mar. Eng.

### THE INSTITUTION OF ELECTRICAL ENGINEERS.

Wireless Section meeting, in the Lecture Theatre of the Institution, on Wednesday, 11th April, 1923, at 6 p.m. (Light refreshments at 5.30 p.m.)

*The Application of a Revolving Magnetic Drum to Electric Relays, Siphon Recorders and Radio Transmitting Keys* (Experimental Demonstration), by N. W. McLACHLAN, D.Sc. (ENG.), Member.

### GENERAL NOTES.

#### BRITISH DYES "BOOM."

NEW PLANT AND AN ORDER FROM GERMANY.

Extensive new plant is being installed at the Huddersfield works of the British Dyestuffs Corporation to meet the growing de-

mand created by the situation in the Ruhr and by a greater public confidence in British acids, intermediates and dyestuffs.

There has recently been a considerable increase in production of acids, intermediates and dyestuffs. This may be due in part to the occupation of the Ruhr, but is due mainly to the strengthening of confidence in the quality and uniformity of British dyes. Dye users, moreover, are always looking for a continuous supply of the right goods almost as much as for the right goods themselves. That is one reason why to-day many of them regard the Reparation material with much less favour than they did twelve months ago.

Inquiries are coming even from the Continent. A week or two ago one came from Brussels for mixed acid, and only the other morning there was another from Germany for nitric acid. This is something absolutely novel for the English chemical industry, and is symptomatic of the general outlook.

In the House of Commons recently, Mr. Short asked the President of the Board of Trade if he could state the total imports of alizarine and other anthracene dyes during the years 1913 and 1922 respectively.

Lieut.-Colonel Buckley, Secretary to the Overseas Trade Department, replied: The imports into the United Kingdom of alizarine and anthracene dyestuffs during the year 1913 amounted to 60,813 cwts., valued at £272,245. In the year 1922 the imports of alizarine dyes amounted to 11,387 cwts., valued at £60,607. Owing to a change in classification which became operative in January, 1920, separate particulars of the imports of anthracene dyes in 1922 are not available.

#### THE PHOTOGRAPHIC FAIR.

The Photographic Fair held at Holland Park Hall, W., from March 15 to 24, was characterised by a good display of exhibits.

Numerous photographic manufacturers showed the latest productions and devices in general apparatus, hand and folding reflex cameras, lenses, new films, ultra-rapid plates, &c. Good specimens of silver nitrate, gold chloride, potassium platinochloride, etc., were exhibited by a well-known firm of manufacturers of photographic chemicals.

Besides these there were also exhibits of radiography, photomicrography, press photography, and colour reproduction. A section on "spirit photography" was arranged by the Editor of *Light*.

Some first-class prints by the professional photographers of other countries were also shown at one stand.

#### PYRIDINE SIMONSENS OIL AND WOOD NAPHTHA.

The Department of Overseas Trade have received a request from a Durban firm to be put in touch with firms in the United Kingdom who are in a position to supply pyridine, simonsens oil and wood naphtha. These materials are required for the denaturing of alcohol for the manufacture of methylated spirits.

The name and address of the applicant, together with further particulars, may be obtained by United Kingdom firms interested upon application to the Department of Overseas Trade, 35, Old Queen Street, Westminster, London, S.W.1 (Room 52). Reference number 10856/ED/CP should be quoted.

#### CZECHO-SLOVAK CHEMICAL INDUSTRY.

In the year 1922 only 50 per cent. of the larger Czecho-Slovak chemical factories were working, and the smaller ones were in more or less the same position. The reason for the small demand lay, as with other branches of industry, in the fact that prices were high owing to fluctuation in the Central European exchanges, German competition, etc., and consumption was consequently restricted, the result being a crisis on the chemical market. One circumstance is common to all these causes, namely, that they are beyond the control of the producer, so that the manufacturer himself can do nothing to remove them. Before the war, the chemical industry in Czecho-Slovakia was in a position to compete with any other, and had a large share in the exportation. Despite the unfavourable conditions of the times, the industry improved its arrangements and methods of business, so that its present constitution in this respect is to-day better than it was.

It is obliged to import most of its raw material from abroad. Thus more especially—pyrite from Spain, phosphate from America, Africa and Australia, salt from Germany and Austria, and fats from overseas. In this way the entire Czecho-Slovak chemical industry, both in its larger and smaller concerns, is dependent on the one hand on the importation of raw material from overseas, while on the other it must endeavour to export the finished products, as there is not sufficient demand for them in Czecho-Slovakia itself.

During the past year the Czecho-Slovak chemical industry aimed at selling off the existing supplies and at covering home consumption, which it is true, was gradually diminishing. The decrease in exports in 1921 is attested by the following statistics, but it should be borne in mind that the value of the Czecho-Slovak crown two years ago was not as high as it is now.

Of the chemical products which have chiefly to be considered, the following exports were effected:—

1920 for	1,480	million	crowns.
1921 for	870	"	"
1922 for	280	"	"

The unemployment figures in the Czecho-Slovak chemical industry for January, 1922, expressed as 686, rose to 2,684 by September, 1922, of which 13 per cent. received doles direct from the State, and 42 per cent. were supported by various industrial concerns. The figures of last quarter are significant: in October there were 2,804 unemployed workmen in the industry, and subsequently in the month of November there is a gradual change for the better, with only 1,626 unemployed. The decrease in wages, which became a necessity last year, was carried through with less difficulty than was anticipated.

In consequence of the rise of prices in Germany, it would seem that Czecho-Slovakia will again be able to supply the demands from abroad, and her chemical industry is to-day actually in a position to compete with England, Belgium, and America in very many articles. As regards its organisation, it should be pointed out that the Czecho-Slovak chemical industries comprise 22 sections, of which each one forms a link between the undertakings of the individual branches of the industry. The entire Union is affiliated to the Central Federation of Czecho-Slovak Industries.

## CZECHO-SLOVAKIA.

### DEMAND FOR BRITISH CHEMICALS.

The Acting Commercial Secretary at Prague reports to the Department of Overseas Trade that the French occupation of the Ruhr district and the present industrial situation in Germany are undoubtedly having their effect on the local market, but the increased demand arising out of the abnormal conditions obtaining in Germany has, as yet, scarcely been noticeable, owing to the fact that the stocks on hand in this country have been sufficiently large to cover all requirements. In view of the general depression in the textile industry, even the demand for aniline dyes has been almost imperceptible, yet in normal times the Czecho-Slovak requirements in dyes were so large as to be an item of great importance even to the largest German works. The present stocks, however, will not last for any great length of time, and there is no doubt that sooner or later there will be a shortage of aniline dyes and higher prices will be seen, especially as German prices have now practically attained the level of those ruling in the international market. The effect of the occupation of the Ruhr on the Czecho-Slovak heavy chemical trade has been to arrest the falling tendency of prices.

Lower prices were expected for acetic acid, soda, borax, and chloride of lime, but in view of the temporary alienation of German competition no reduction whatever has taken place, and local prices are still two or three times higher than German prices, and often higher than those ruling in the Western States.

Following are the market prices of chemicals per kilo ruling in Prague on the 8th March:—

	Czech Crowns.
Acetone .....	21.00
Alum .....	4.35
Formic Acid (80 per cent.) ....	12.30
Benzoic Acid .....	38.00
Sulphate of Magnesia .....	1.40
Borax Crystals .....	6.50
Boric Acid .....	11.00
Chloride of Barium .....	3.20
Chloride of (chlorinated) lime	2.60
Chloride of Potassium .....	10.00
Chrome Alum .....	7.00

## Czech Crowns.

Dextrin .....	3.00
Green Vitriol or Copperas .....	0.60
Acetic acid 80 per cent. ....	18.00
Yellow cyanide of Potassium .....	30.00
Sulphate of Soda (powder) ...	0.90
Sulphate of Soda (crystals) ....	0.80
Permanganate of Potash .....	15.00
Nitrate of Potassium .....	7.00
Oxalate of Potassium .....	19.00
Blue Vitriol .....	8.00
Lime .....	8.00
Oxalic Acid .....	13.00
Paraffin .....	3.50
Sal Volatile 98/100 .....	5.90
Liquid Ammonia 0.910 .....	5.30
Nitric Acid 36° Be .....	3.00
Hydrochloric acid 20-22 p.c. ..	0.95
Shellac T.N. Orange .....	64.00
Sulphide of Sodium .....	3.80
Sulphide in pieces .....	1.80
Sulphuric Acid 66 per cent. ...	1.25
Tartaric Acid .....	25.00
Turpentine (French) .....	19.50
White Vitriol .....	2.80
Japan Wax .....	12.50
Carnauba Wax .....	16.00

In the House of Commons, Mr. Darbishire asked the President of the Board of Trade if he had received a communication from the British Chemical Trade Association, which was addressed to the Secretary of State for Foreign Affairs and passed on to him, containing proposals for the setting up of a licensing office in the Cologne area, which should be competent to deal with all consignments of British goods consigned to the United Kingdom or elsewhere overseas on British firms' account; and, if so, did he intend to endeavour to get it adopted by the Inter-Allied Rhineland High Commission?

Lieut.-Colonel Buckley said that he had received the communication referred to. There were three licensing offices (Bad Ems, Dusseldorf, and Essen) dealing with their respective areas. To set up a fourth at Cologne dealing with British trade would add to the confusion.

## DEATH OF SIR JAMES DEWAR.

By the death of Sir James Dewar, F.R.S., the world in general and physical science in particular are the poorer.

His work on the liquefaction of air, nitrogen, oxygen, hydrogen, etc., represents one of the many great scientific achievements of the last century. This work led up to his invention of the vacuum flask which bears his name, and which was adapted to every-day domestic use in the form of the Thermos flask.

These discoveries not only led him into further investigations, but also prompted others to follow along lines which were only possible as a result of his work.

He was for many years, and until his death on March 27, connected with the Royal Institution, at whose meetings many of his discoveries were first announced. Here he followed and maintained the illustrious examples of great predecessors. Almost all the important scientific societies throughout the world have honoured him at some time or another.

NAPHTHENIC ACIDS FROM  
JAPANESE PETROLEUM.

BY Y. TANAKA AND S. NAGAI.

On acidifying the waste lye from the refining of 25-26° Be petroleum distillate, a thick brown oil S.G. 0.9853 and acid value 68.8, sulphur content 0.89 per cent. was obtained. It emulsified with water, and gave an ether soluble copper salt indicative of naphthenic acids. Other compounds were, however, present. The naphthenic acids were separated and purified by hydrolysis of their methyl esters, the final product being a light yellow viscous liquid, S.G. 0.9918, refractive index 1.4824, acid value 254.3, mean mol. wt. 221, iodine value nil. By careful fractionation of the methyl esters, trideca, tetradeca, and penta decanaphthenic acids were isolated.—(From *J. Amer. Chem. Soc.*, 1923, XLV., 754-6.)

## CORRESPONDENCE.

## THE AUTHENTICITY OF THE LATIN WORKS OF GEBER.

To the Editor of THE CHEMICAL NEWS.

SIR,—I was much interested to read Mr. E. E. Whale's letter on the above topic, in your issue for March 9, and the excellent report of Mr. Holmyard's lecture on "Arabian Alchemy and Chemistry," which appeared in the previous issue. In that report you were kind enough to include my own remarks—to which I would draw Mr. Whale's attention—which perhaps sufficiently define my own position towards the question of Geber in the light of Mr. Holmyard's researches; but it may possibly be of use if I briefly expand these here. Like Berthelot, I know no Arabic, and in common with him and other writers on the history of chemistry, I had to rely, when writing *Alchemy: Ancient and Modern*, upon the translations of Geber's original works, which Berthelot had had prepared for the purposes of his own studies. Judging from these, no other conclusion seemed possible than that which Berthelot himself drew, namely, that the Latin words ascribed to Geber are spurious. For, whereas these Latin works are definite and practical treatises, the Arabic works are highly mystical in character. Moreover, these latter works make no mention of the famous sulphur-mercury theory of the metals which play so important a part in the Latin works. Mr. Holmyard, it is true, in controverting this argument, has not produced the Arabic originals of the Latin works; but he has discovered other Arabic MSS. the undoubted work of Geber—such as *The Book of Properties* in the British Museum—which are exactly like these in character; works which describe many practical preparations and make mention of the sulphur-mercury theory; and he suggests that the Arabic MSS. of Geber's which Berthelot had translated were not the *chemical* works of Geber, but religious works in which Geber—as a chemist—naturally made use of chemical symbolism.

I entirely agree with Mr. Whale that it is highly desirable that adequate translations should be made of the various Arabic MSS. in question, and it is to be hoped that Mr. Holmyard might be persuaded to undertake

this important work. A translation of Geber's *Book of Properties*, for example, the MS. of which is in the British Museum, would be especially welcome. Until such translations have been made it may be as well to retain an open mind concerning the question of the authenticity of the Latin works; but certainly the evidence for reversing the decision arrived at by Berthelot, which Mr. Holmyard has already put forward, is, to my mind, very convincing.

As to the different spellings, "Geber" and "Dschabir," these are merely different transliterations of the same Arabic name, and do not refer to different individuals.—Yours, etc.,

H. STANLEY REDGROVE,  
B.Sc., A.I.C., F.C.S.

191, Camden Road, N.W.1.  
March 10, 1923.

[Owing to an error on the part of the printers, a portion of Mr. Redgrove's letter, which appeared in the issue of March 23, was inadvertently omitted. We publish above the letter in full, and tender apologies to Mr. Redgrove and our readers.—Ed., C.N.]

## NOTICES OF BOOKS.

*Glue and Gelatin*, by JEROME ALEXANDER. Pp. 236. New York: The Chemical Catalog Co. Inc., 19, East 24th St. 1923. Price 3 dollars.

The publication of this monograph under the direction of the American Chemical Society is well justified from the points of view of the principles of physical chemistry which it touches and the industrial importance of these substances as well as by their long use.

The subject is a difficult one. Much information is scattered through the scientific literature, but often under unexpected headings.

Another difficulty that the author must have encountered is the unequal quality of the work published, especially concerning their colloidal properties.

Most attention has here been devoted to well known theories which are expounded and discussed in the light of the properties

of glue and gelatin, and especially with reference to recent work on the latter.

In the chapter on their chemistry, the different estimations and calculations of the molecular weight of gelatin are given. It is interesting to note that the most recent computation puts this at about 10,300.

With regard to the testing of glue and gelatin, it is pointed out that no single test can satisfactorily grade a commercial sample. Many tests are necessarily of an empirical nature, and this must continue until a more exact knowledge of the chemical constitution of these bodies is forthcoming.

There are, however, certain specifications that can be determined and must be complied with in the case of gelatin intended for human consumption.

This raises the question how to distinguish gelatin from glue; there is, in fact, no sharp distinction. But gelatin for food must not contain, e.g.,  $\text{SO}_2$ , As, Cu, Zn, or indeed, any injurious body.

The author is to be congratulated on this compilation, of interest both to technologists and physical chemists.

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*Anorganische Chemie*, von Dr. F. EPHRAIM. Zweite und dritte verbesserte Auflage. Pp. VIII. + 742. Dresden and Leipzig: Verlag von Theodor Steinkopff. 1923. Price unbound 8s. 6d., bound 10s. 2d.

There are now so many textbooks on Inorganic Chemistry that there seems little need for new publications covering the general theory and description of this subject.

Prof. Ephraim has, however, written one which has gone through two or three editions in the course of a few months, from quite a new standpoint, and which deserves the attention of chemists, and certainly has justified the publication of yet another *Inorganic Chemistry*.

This readable volume opens with an account of the present views concerning the structure of the atom, followed by a brief description of the elements and general chemical theory. The essential principles of physical chemistry are included.

In the next chapter, the compounds of the halogens are described, beginning with those with hydrogen. The hydracid salts,

the oxides, oxy-acids, and compounds of the elements with one another complete this section.

Chapter three deals with the oxides of hydrogen, of the metals, and the acidic (higher and amphoteric) metal oxides. Following are chapters on the other elements in convenient groups. The mode of treatment is along the same lines, viz., first the hydrogen-compounds, then the oxides and salts, and finally the halogen and cyanogen compounds are described.

The inter-metallic compounds and metal hydrides, the rare earths, and the radioactive bodies all have separate chapters allotted to them.

By this arrangement the periodic system and other generalisations are made apparent.

Prof. Ephraim's stimulating and comprehensive volume could well be of service to those advanced science students studying German. Advanced workers and lecturers in inorganic chemistry will certainly notice many interesting points in connection with the mode of presentation of even the most recent developments in chemistry.

J.G.F.D.

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*The Chemical Technology and Analysis of Oils, Fats and Waxes*, by Dr. J. LEWKOWITSCII, M.A., F.I.C. Sixth edition, entirely. Revised by G. H. WARBURTON. Vol. III., pp. VIII. + 508. London: Macmillan & Co., Ltd., St. Martin's Street, W.C. 1923. 36s. net.

The publication of Vol. III. of Dr. Lewkowitsch's compendium on Oils, Fats and Waxes, now revised and brought up-to-date by Mr. Warburton, completes the sixth edition of this well-known standard work of reference; Vols. I. and II. having appeared last year.

The appearance of Vol. III. has been awaited somewhat impatiently by those who have had frequent occasion to consult this work, since it contains the subject index of the whole edition.

The matter of this volume, in addition to useful statistics and tabular information, contains much that is valuable to technical chemists, analysts and others requiring authoritative information on this important

and ever-expanding branch of industrial chemistry.

The British Association for the Advancement of Science have issued as a reprint the Report on *Absorption Spectra and Chemical Constitution of Organic Compounds*. The Committee responsible for the report consisted of Prof. I. M. Heilbron, Prof. E. C. C. Baly, and Prof. A. W. Stewart; and they have collected and reported upon the experimental work and theories put forward by numerous investigators in this field.

*Readable School Chemistry*, by J. A. COCHRANE, B.Sc. Pp. XI. + 84. London: G. Bell & Sons, Ltd., Portugal St., W.C.2. 1923. Price 2s.

Few elementary chemistry textbooks really appeal to young pupils just beginning the subject.

It is not proposed to enter into the causes of this here, beyond stating that Mr. Cochrane has written a volume which will appeal to them. The subject is developed historically, and the book is evidently intended to supplement the practical work; each chapter should naturally be studied after the experimental work has been completed.

The gradual development of chemistry as it is to-day, is traced in a manner calculated to sustain and stimulate the interest of beginners. In particular, the chapters on *Burning and Rusting* and *The Air and its Constituents*, are especially well written for schoolboys.

On p. 3 the author accurately indicates that the alchemical period dates from the Christian era to 1500 A.D., and not from earlier times. (Yet on p. 7 it is stated that "Egyptians practised alchemy five or six thousand years ago.")

This little volume can be warmly recommended for those scholars for whom it is intended. It would also be of service to those who do not intend to pursue the subject very deeply. The inclusion of several plates of historical and general interest, and its low price, are additional recommendations.

J.G.F.D.

*The Mathematical Theory of Relativity*, by A. S. EDDINGTON, M.A., M.Sc., F.R.S. 10½ins. x 7½ins. Pp. X. + 247. Cambridge: The University Press. Price 20s. net.

*The Mathematical Theory of Relativity*, by A. KOPFF. Translated by H. LEVY, M.S., D.Sc., F.R.S.E. 7½ins. x 4½ins. Pp. VIII. + 214. London: Methuen & Co., Ltd., 36, Essex Street, W.C. Price 8s. 6d. net.

Whereas, during recent years a very large number of popular expositions of the theory of relativity have appeared, English and American students desirous of really mastering the subject have been saddled with the double task (except as concerns the help afforded them by the translations of papers by Einstein and Minkowski, which were published in 1920 by the University of Calcutta) of studying a difficult subject in a foreign language. So great was the need that it might be said that almost any book dealing with the mathematics of the theory of relativity would be welcome. Especially welcome indeed, then, is this brilliant treatise by Professor Eddington, and not less so is the very readable translation of Professor Kopff's fine work. In many ways the two books show marked differences in the treatment of their subject matter; and each has an excellence characteristically its own. Professor Eddington's book is, perhaps, the more philosophical, as it is also the more novel in its mode of presentation; but, on the other hand, it is the more difficult to read and to master. The fact that it forms in a manner, a sequel to the author's previously published *Space, Time and Gravitation* accounts for its somewhat brief treatment of the restricted theory of relativity, which is dealt with very fully in Professor Kopff's work. Both books contain chapters devoted to the tensor calculus, which forms the necessary mathematical apparatus for dealing with the generalised theory, to a discussion of which, its various aspects and consequences, both books then pass. Professor Eddington's treatment is the fuller here—the problems of the curvature of time and space and of world-geometry generally being discussed at considerable length with special reference to the views of Einstein, de Sitter and Weyl. Two points made clear in the "Introduction" to Professor Eddington's book must not be passed over in this all too short

notice. One is that the physical qualities dealt with by science are essentially *manufactured articles*. "Physical quantities," he writes, "are not properties of certain external objects, but are relations between these objects and something else." The second point is that an intrinsic property of a measuring instrument must appear as a uniformity in a series of measurements made by it, and that it is just such uniformities which constitute what are called "laws of nature." The philosophical importance of such inevitable conclusions of the theory of relativity as these can hardly be underestimated.

Both these books can be unreservedly recommended to students. To read and to master one of them is to gain a very good working knowledge of the greatest scientific achievement of the present century. But certainly the student who is keen will not be content with this. He will read and master them both. H. S. REDGROVE.

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### BOOKS RECEIVED.

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*The Spectroscope and its uses in General Analytical Chemistry*, by T. THORNE BAKER, A.M.I.E.E., F.R.P.S. Pp. X. + 208. Second Edition. 1923. Messrs. Baillière, Tindall & Cox, 8, Henrietta Street, Covent Garden, W.C.2. 7s. 6d. net.

*The Phase Rule and its Applications*, by ALEXANDER FINDLAY, M.A., PH.D., D.Sc. Pp. XVI. + 298. Fifth Edition. 1923. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 10s. 6d. net.

*Laboratory Manual of Physical Chemistry*, by ALBERT W. DAVISON and HENRY S. VAN KLOOSTER. Pp. VIII. + 182. 1922. Messrs. Chapman & Hall, 11, Henrietta Street, Covent Garden, W.C.2. 10s. net.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 6861—Booer, J. R.—Preparation of salts of boric acid. March 9.
- 6737—British Dyestuffs Corporation Co., Ltd.—Manufacture of formaldehyde or its polymers. March 8.
- 7009—Consortium Fir Elektrochemische Industrie Ges.—Manufacture of anhydrides of fatty acids. March 10.
- 6598—Techno-Chemical Laboratories, Ltd.—Separating solids from liquids. March 7.
- 6596—Weber, W.—Process for treating ammonium chloride lyes in iron vessels. March 7.
- 7747—Aktieselskabet Hydropeat.—Manufacture of colloidal solutions of ferric oxide. March 17.
- 7770—British Cellulose & Chemical Manufacturing Co., Ltd.—Treatment of cellulose acetate, etc. March 17.

#### Abstract Published this Week.

- 191854—Dyes.—Soc. of Chemical Industry in Basle; Basle, Switzerland.

*Triarylmethane dyes* are obtained by condensing phenyl-chloroform or a substitution derivative or homologue thereof, or 1-chloro-2-naphthyl-chloroform, with naphthol or a substitution product thereof having a free 4-position, in presence of a substance neutralising acid; addition of a catalyst, for instance copper or alcohol, is advantageous. The dyestuffs derived from 1-naphthol-2-carboxylic acid dye wool grey tints changed by afterchroming to green or blue tints fast to fulling and potting; they may also be dyed or printed on chrome-mordanted fabrics, or used in single-bath processes. According to examples dyestuffs are obtained from  $\alpha$ -naphthol and phenyl-chloroform in the presence of caustic soda, and from 1-naphthol-2-carboxylic acid and phenyl-chloroform in presence of copper powder and caustic soda, lime, or magnesia. The several chlorophenylchloroforms, and the sulpho derivatives of 1-naphthol-2-carboxylic acid, such as 1-naphthol-7-sulpho-2-carboxylic acid are also mentioned as suitable components.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

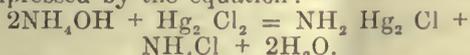
VOL. CXXVI. No. 3287.

## THE INTERACTION OF AMMONIUM HYDRATE AND MERCUROUS BROMIDE.

By J. G. F. DRUCE, M.Sc. (LOND.),  
R.NAT.DR. (PRAGUE).

Some time ago, on account of its theoretical and photographic interest, the action of ammonium hydrate upon mercurous chloride was quantitatively investigated (see *The Chemical News*, 1921, CXXIII., 153).

It was concluded that the results were expressed by the equation:—



The action of ammonium hydrate upon mercurous bromide has now been examined in a similar manner.

For this purpose mercurous bromide was prepared by precipitating an acidified solution of mercurous nitrate with slight excess of potassium bromide. The almost white precipitate was filtered off with the aid of a filter pump, and washed repeatedly with warm water to remove any potassium nitrate or acid adhering to it. It was finally drained and dried.

0.9380 gram was placed in a stoppered flask with about 25 cc. of water. Twenty cc. of a normal solution of ammonium hydrate were added. The stopper was replaced, and the mixture was shaken for a few minutes and allowed to stand for two days. The black residue was then removed as quickly as possible by filtration, and was washed with distilled water. Filtrate and washings were made up to 200 cc.

The residual ammonia was estimated by titrating lots of 20 cc. of this diluted filtrate with decinormal hydrochloric acid. The average volume of acid required in these experiments was 16.7 cc., which corresponds with 0.5836 gram ammonium hydrate in the whole filtrate. Therefore 0.1164 gram had reacted with the mercurous bromide.

The quantity of ammonium bromide formed was determined by taking three lots of 20 cc. of the diluted filtrate obtained above and boiling for five minutes to expel the free ammonia. This solution was then

titrated with fiftieth normal silver nitrate solution. The average volume required in the three experiments was 8.35 cc., which indicates that the total filtrate contained 0.1632 gram ammonium bromide.

Thus, 0.1164 gram of ammonium hydrate reacted with 0.9380 gram of mercurous bromide, forming 0.1632 gram of ammonium bromide.

These results indicate that two molecules of ammonium hydrate act on one of mercurous bromide and one molecule ammonium bromide is produced.

The other product of this interaction was the "black precipitate," which could be  $\text{NH}_2\text{Hg}_2\text{Br}$ , or a mixture of  $\text{NH}_2\text{HgBr}$  and finely divided mercury.

At the end of the article previously cited, the same question was considered in connection with the corresponding chloro-compound, and the conclusion was drawn that the substance was a compound, since it did not appear to amalgamate with copper.

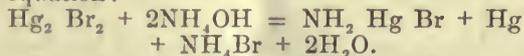
The black precipitate obtained in these experiments amalgamated readily when rubbed on a bright piece of pure copper when freshly prepared.

When washed quite free from ammonia it did not amalgamate so readily, and when dry, amalgamation was still more difficult but could, nevertheless, be effected.

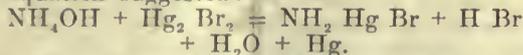
This strongly suggests that the black precipitate is a mixture.

Additional support for this has been obtained by boiling the substance with a strong solution of ammonium bromide. By this means the free mercury was obtained in the form of a fair-sized globule, whilst the white mercuric bromo-amide,  $\text{NH}_2\text{HgBr}$ , dissolved. This latter substance crystallised out when the hot saturated solution cooled.

Thus it has been established that when ammonia acts upon mercurous bromide, the reaction may be expressed by the equation:—



It was thought of interest to ascertain whether by using excess of mercurous bromide with ammonium hydrate, any free acid could be liberated as the following equation suggested:—



With this in view, 3.5 grams mercurous bromide were ground up in a mortar with

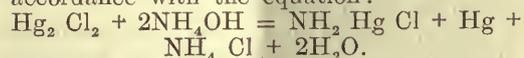
20 cc. of water and 5 cc. of normal ammonium hydrate. When drops were tested with phenol-phthalein, methyl-orange, and litmus, all three indicators showed that the mixture was neutral, therefore no free hydrobromic acid could have been formed.

Since it was clearly proved that the insoluble product of the interaction of ammonium hydrate and mercurous bromide was a mixture of mercury and mercury bromo-amide, it was deemed important to further investigate the corresponding product from mercurous chloride.

On careful examination it was found that the wet "black precipitate" just as it was prepared, readily amalgamated with pure copper, but less readily when free from ammonia and least easily when dry.

Finally, when this "black precipitate" was boiled with a strong solution of ammonium chloride the mercury ran together to form one globule, whilst on cooling the supernatant liquid it deposited the infusible white precipitate.

The reaction between ammonium hydrate and mercurous chloride is thus in accordance with the equation:—



The International Institute of Agriculture, Rome, has issued a communication comparing the world's crops of 1922 with pre-war figures.

The statistics collected indicate that the production of maize in Europe is now only 62 per cent. of that grown annually before the war. The world's vintage is 21 per cent. above the average 1909-1913 figure.

Other important data are given.

#### CALCIUM ARSENATE FOR THE U.S.A.

The Commercial Counsellor at Washington (Mr. J. J. Broderick) reports that three firms of wholesale druggists in New Orleans are desirous of receiving samples and quotations for the supply of calcium arsenate. One of the firms also desires to import arsenic as well as Paris green.

Further particulars, together with the names and addresses of the applicants, may be obtained by United Kingdom firms on application to the Department of Overseas Trade (Room 52).

#### VALENCY.

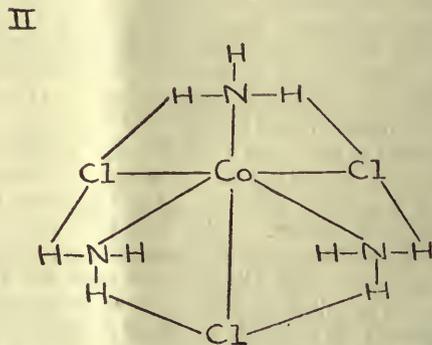
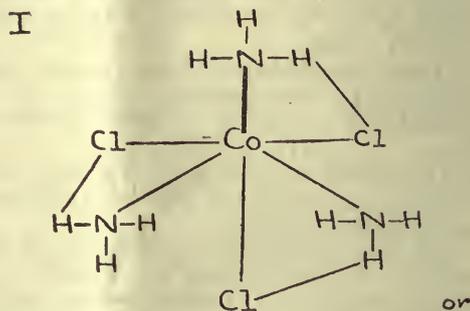
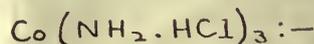
BY WILLIAM R. FIELDING, M.A., M.Sc.,  
(VICT.).

Senior Science Master, King Edward VII.  
School, Lytham.

(Continued from Page 214.)

*The Cobaltamines.*

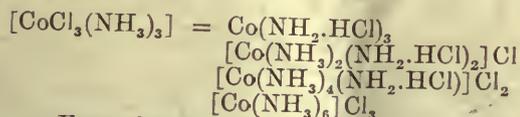
$\text{CoCl}_3(\text{NH}_3)_3$ , which is non-ionisable, may be written thus:—



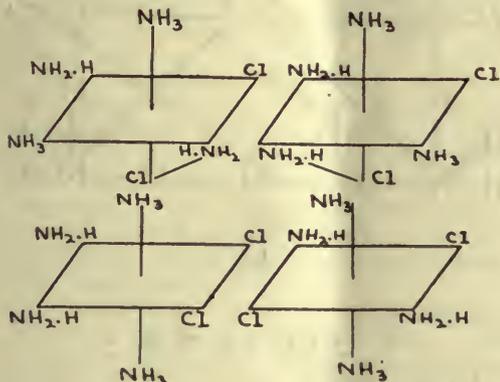
(Fig 3b)



As the chlorine is linked up with hydrogen as well as cobalt, neither the chlorine nor the nitrogen are exerting their maximum "pull" on the cobalt, and the latter is open to the attack of other negative groups. Each additional ammonia molecule breaks up a ring (two rings in the second formula), and the heat-change affects the valency of everything in the complex molecule. The action of successive molecules of ammonia may be represented thus:—

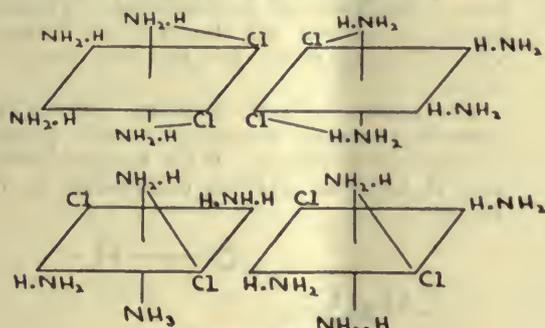


From formula I. in Fig. 36, four isomers of  $[\text{Co}(\text{NH}_3)_4]\text{Cl}_2$  could be secured thus:—



(Fig 37)

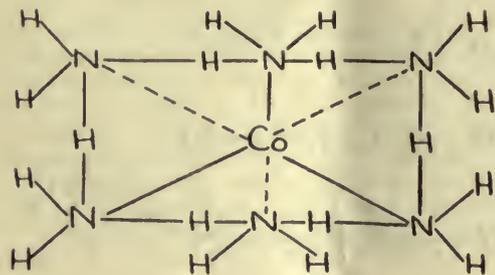
and from formula II. in the same Fig. four isomers (two being mirror-images), thus:—



(Fig 38)

If the  $\text{NH}_3$  acts as a single unit and not as  $\text{H.NH.H}$  and  $\text{NH}_2\text{.H}$ , the last two are alike, as are also the two former.

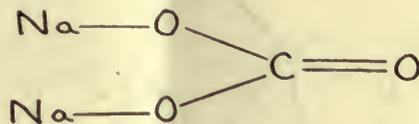
When all the chlorine has been replaced by ammonia the final form will present the following appearance (a plane figure is used to show valencies only):—



(Fig 39)

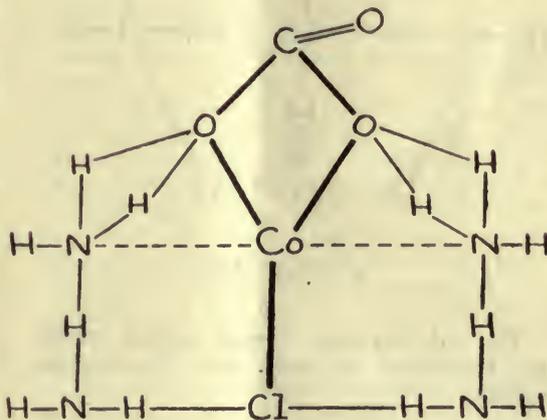
Co is hexad; nitrogen is pentad in three cases and tetrad in three other cases; it can become pentad all round by joining direct to the central atom. Cobalt will then have a valency of nine, six joining electro-negative nitrogen atoms, and three joining electro-negative chlorine atoms. This high valency is, in a way, a kind of reflected glory, and owing to borrowing electrons from the six electro-negative nitrogen atoms it is able to ionise the three chlorine atoms.

A similar procedure is adopted in evolving the formula of cobalt pentammine containing the  $\text{CO}_3$  group. In carbonates (Fig. 40) the metal is not joined directly to the carbon.



(Fig 40)

Four molecules of ammonia combine with the  $\text{Co}(\text{CO}_3)\text{X}$ , thus:—

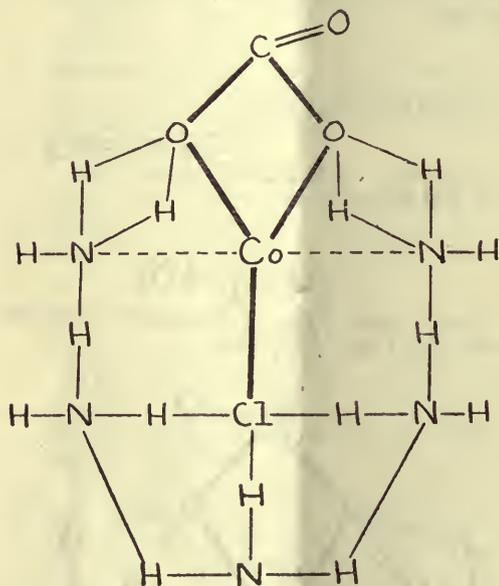


(Fig 41)

Here Co is triad, nitrogen triad and tetrad, hydrogen dyad and monad, oxygen dyad and tetrad, and chlorine triad. The two tetrad nitrogen atoms are each joined to three hydrogen atoms which are functioning as dyads; these three atoms will not utilise as much of the valency-strength of the nitrogen atom to which they are at-

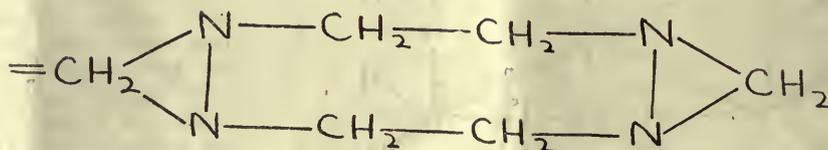
tached as the three atoms of hydrogen in  $\text{NH}_3$  do; these N atoms are thereby able to effect linkages with the cobalt which is likewise not extended to its full valency-capacity because it is joined to three atoms which are functioning as tetrads and triads, their usual valencies being dyad and monad respectively. These two nitrogen atoms may, and probably do, connect up with the cobalt, and the valencies are shown in dotted lines.

The fifth ammonia can now be added, and it tackles the chlorine end of the molecule. The following formula is suggested:

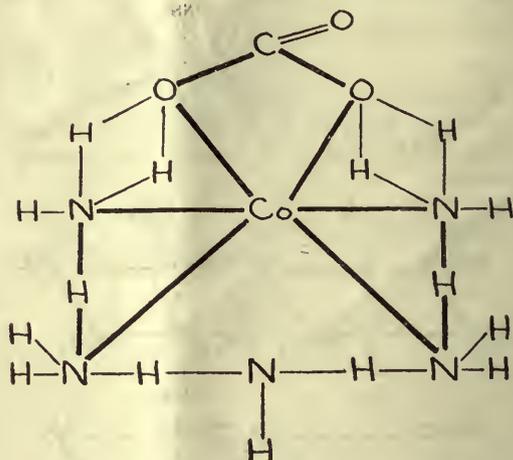


(Fig 42)

The chlorine atom is now ionised, when the following redistribution of valencies occurs:—



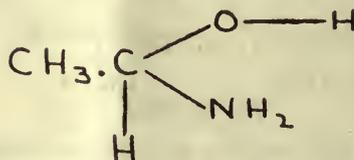
(Fig 45)



(Fig 43)

An alternative method would be to group the  $\text{NH}_3$  molecules without attempting to explain how two pentavalent nitrogen atoms link each other. Nitrogen would be pentavalent throughout, and bonds numbers 1 and 2 would be cancelled. (These bonds, which are not shown in the figure, join the cobalt atom and the two lower N atoms.)

The group  $=\text{C}=\text{O}$  behaves differently towards ammonia according to the group to which it is joined. With acetaldehyde, etc., it forms an addition compound, as in Fig. 44.



(Fig 44)

and with formaldehyde, hexamethylene-tetramine (Fig. 45):—

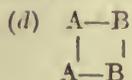
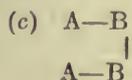
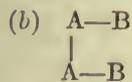
## CONCLUSIONS.

(1) Valency is a variable property of elements, the variability depending on the element, the temperature, the pressure, and the element or elements with which it is combined.

(2) In many simple chemical actions the Law of Conservation of Principal Valencies holds, the temperature remaining constant; but

(3) In an exothermic action the degree of polymerisation is greater than the average calculated from the constituents. That is, as the amount of energy in the system is reduced the degree of polymerisation is increased. This is in agreement with the known facts that  $p$  is reduced as temperature rises, except in the case of endothermic compounds.

(4) As  $p$  is increased the usual valency of elements must be increased also. This may be explained by the following linkages:



(5) Where two electro-positive or two electro-negative atoms are linked together, one may be regarded as electro-positive to the other, this being effected by a change in the electronic orbits or by the nuclei attracting each others free electrons.

(6) By carefully selecting the most suitable conditions of temperature, pressure, elements, etc., and making use of the changes in valency following every physical and chemical change and also by judicious "loading" of the central atom, valencies can be increased beyond those generally associated with the element. As Co, Pt, Cr, etc., can be joined to six atoms or groups as well as to several atoms which are ionised in solution, their valencies in the solid state (where some degree of poly-

merisation will almost certainly take place) will be considerably higher than the number of the group to which these elements belong in the Periodic Table. Their valencies may be reduced by supposing that the co-ordinated elements exert a single resultant valency towards the central atom.

(7) When compounds decompose on heating, melting, or boiling, the valency of the two elements for each other must be zero at that particular temperature and pressure.

(8) Several instances have been given where it is suggested that an atom "compensates" or "accommodates" another atom in the matter of electrons. Thus hydrogen often functions as a dyad, where its electron may be supposed to be shared between two electro-negative atoms.

January 17th, 1923.

#### THE INFLUENCE OF HUMIC ACIDS ON THE ASSIMILATION OF PHOSPHORIC ACID.

By K. MACK.

Phosphoric acid occurs in the soil in the form of primary, secondary and tertiary phosphates of the alkalies, alkaline-earth metals, aluminium, iron and manganese. It is perhaps also present as the tetraphosphate of certain metals. The water of the soil which contains phosphate ions becomes separated from the insoluble phosphates through the action of calcium, magnesium, aluminium and iron-hydrates, magnesium and iron-carbonates and certain silicates. Through the activity of soil bacteria, which, during respiration, produce carbon dioxide and, in disintegrating organic substances, produce acetic, lactic, butyric, and valeric acids, the insoluble phosphates become partly soluble again. In soils rich in organic substances, a large quantity of humic acids is formed which renders the phosphates soluble. Phosphoric acid is found in the soil not only as a mineral, but also in the form of organic compounds, such as phosphatids (lecithin), phytine and nucleoproteids, as is shown by the work of Stoklasa and others. These organic combinations are due to the remains of plants incorporated in the soil (stubble, roots, etc.). Stoklasa observed that the phosphoric acid combinations found in the soil are much more energetically assimilated, under the action of bacteria, than pure insoluble phosphates. He also concluded that the soil contains other forms of phosphates than those recognised

hitherto, notably easily-assimilated humo-phosphates.

The writer has made a series of experiments with the object of determining the effect of humic acids on the various phosphates. The acid used was extracted from peat, which was treated with sulphuric acid to separate the alkaline humates: 10 grs. of pulverised "humic" acid were added to a quantity of phosphate corresponding to 0.01 gram-molecule of phosphoric acid and the whole was left for 48 hours in a litre of water, and was frequently stirred. The results proved that humic acids render soluble the following quantities of phosphate, expressed in per cent. of phosphoric anhydride: 29.45 per cent. of di-calcium phosphate, 28.46 per cent. of tri-calcium phosphate, 12.54 per cent. of tertiary aluminium phosphate, and 7.46 per cent. of tertiary iron phosphate. Humic acids therefore dissolve insoluble phosphates. They act on di-calcium phosphate in the same way as on tri-calcium phosphate.

Humic acids act differently when alkalis are present. Thus, humate of ammonia renders soluble less tri-calcium phosphate than in the former case (23.08 per cent.  $P_2O_5$  as against 28.46 per cent.), but, on the other hand, much more tertiary aluminium phosphate (23.77 per cent., as against 12.54 per cent.), and tertiary iron phosphate (20.37 per cent., as against 7.46 per cent.).

With metallic oxides, humic acids and humates are capable of forming complex combinations, containing the metal in the anion. Thus, ammonium humate may combine with aluminium and iron phosphates to form compounds containing, besides iron and aluminium, phosphoric acid, otherwise known as salts of a "humophosphoferric" acid and a "humophosphoaluminic" acid. Pure humophosphoferric acid has been isolated; it is a bituminous, blackish-brown substance, soluble in alcohol up to 2.65 per cent.

In a soil rich in bone and lime phosphates only 3.5 per cent. of phosphoric anhydride were found to be present, which agrees with the fact that marshy soils rich in lime are not very fertile. From a garden rich in mineral and organic fertiliser, 25.27 per cent. of anhydride were obtained.

The excess of bases over phosphoric acid shows that the latter is present especially as a basic phosphate. In soils with an alkaline reaction, aluminium and iron phos-

phates are combined with the humic basis, which explains their greater fertility.

Humophosphoferric and humophosphoaluminium acids therefore serve to supply plants with phosphoric acid, and perhaps with iron and aluminium in a form which can be easily assimilated. This was fully confirmed in a series of experiments in which beets were cultivated in various nutritive solutions, of which some were exclusively mineral while others contained humate of ammonia. After 18 days, there was still considerable quantity of phosphoric acid in the first solutions, while the second contained no further traces. Other experiments are being made. Already preparations of peat and ashes used as fertilisers, and the addition of iron hydrate to the ordinary fertilisers have given good results.

The writer concludes by saying that greater importance should be attached to raw phosphates containing oxide of iron, such as those of Bavaria and the Hartz mountains; he is not in favour of the use of superphosphates, which eventually render the soil too acid. The use of manure, on the other hand, should be widely developed. In regions where, from climatic or economic reasons, it is impossible to rear live-stock, peat may be used with advantage, for it not only renders phosphoric acid assimilable, but also furnishes nitrogen, and is a good medium for bacteria.—(From the *Chem. Zeit.*, XLVI., pp. 73-5.)

#### GENERAL NOTES.

##### GERMANY'S POTASH INDUSTRY.

An extract forwarded to the Department of Overseas Trade by the Commercial Secretary at Cologne states that a number of potash works in Central Germany have been compelled to restrict work owing to unfavourable sale conditions. During 1922 boom conditions prevailed on the potash market, but in January of this year sales had already weakened, and the sale figures did not equal those of January, 1922. Fears were expressed that inland business would suffer a considerable decrease this year. These fears have now been realised. The German agricultural industry has greatly restricted its orders during the past few weeks, and in part has stopped them altogether, the cause of which is to be found in the disparity between the costs of

production and the sale prices for agricultural products.

It was to be foreseen that the improvement of the mark and the accompanying price reduction would also have its dark side. In the interests of guaranteeing food supplies, special attention will in the near future have to be given to agricultural conditions. The price reduction in corn, potatoes, etc., is in no proportion to the reduction in the costs of production, and landowners are, therefore, no longer in a position to devote the same expenditure as heretofore to the supply of artificial manure.

It goes without saying that the potash industry has been hard hit by the decline of the inland demand, and a great number of potash works have had to restrict work. Export sales do not recompense for the loss of the inland business. The potash business with America has not justified expectations, and it is, moreover, reported that the Aisatian potash works are doing their best to obtain the American market, and are under-bidding. The American farmer is, therefore, assuming a certain aloofness, expecting no doubt that the German potash works will also soon be compelled to reduce their prices.

The price question is to-day, in fact, the essential point in the sale problem. On the one hand, should the present prices be retained, there is no hope of increasing sales, and the closing down of works will be unavoidable. A reduction, on the other hand, endangers, in view of the increased costs of production and especially in view of the increased wages, the financial basis of the potash industry, which has only just been re-established. As, however, in the present conditions, the economic policy of the various industrial groups is dictated in the first place by general economic reasons, the potash industry will no doubt decide upon a reduction of its prices, in order to revive inland sales.

#### THE ECONOMIC POSITION IN CZECHO-SLOVAKIA.

The British Vice-Consul at Prague (Mr. J. W. Taylor) has forwarded to the Depart-

ment of Overseas Trade a survey of the industrial situation in Czecho-Slovakia, by Dr. Hodac, the Secretary-General of the Federation of Czecho-Slovak Industrials. Dr. Hodac's statements are always carefully considered.

An improvement has taken place in the sale of coal and coke, in the output of pig-iron, steel and rolled-iron manufactures. At the end of December, three blast furnaces were in operation; to-day seven are being worked; but even now no less than 15 are idle. This improvement is connected with special temporary causes.

On the other hand, unemployment in the engineering trade has shown no improvement.

In the chemical industry, a bigger demand for sulphuric acid has been noted in connection with the use of coke. Those branches of industry which were doing comparatively well last autumn, and which felt the crisis only later, viz., the varnish factories and the technical chemical industry, are now feeling the slump in the same way as the colour factories do. Employment in the wood pulp industry is good; in the paper industry it has improved somewhat in regard to a few kinds only. There has been a considerable demand for leather of all kinds.

The position in the glass industry remains unfavourable. In the window glass branch there are about 900 workmen employed out of 5,000. In the bottle factories 700 workmen are employed, instead of 3,500. In the mirror and cast glass factories only 1,440 workmen are employed out of 2,400. At the end of December the number of workmen employed in the manufacture of hollow glass was 7,864, and in February 8,375, but the normal number is 20,000.

Lieut.-Colonel Buckley informed Mr. Graham White that the following statement showed, for each of the years specified, the quantity and the declared value of the imports into the United Kingdom, registered as consigned from the United States of America, of intermediate coal tar products used in the manufacture of dyes, and of finished dyestuffs obtained from coal tar, respectively:

Description.	1920.		1921.		1922.	
	Quantity. Cwts.	Value. £.	Quantity. Cwts.	Value. £.	Quantity. Cwts.	Value. £.
Intermediate coal tar products used in the manufacture of dyes (including aniline oil and salt and phenyl glycine) .....	44,527	736,221	1,324	27,891	1	8
Finished dyestuffs obtained from coal tar	15,636	532,897	1,218	35,576	150	1,444

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

The Friday evening discourse on April 13 was delivered by W. H. ECCLES, D.Sc., F.R.S., M.I.E.E., M.R.I. His subject was *Studies from a Wireless Laboratory*.

On Monday, April 9, the General Meeting was held.

#### ROYAL SOCIETY OF ARTS.

The Cantor Lecture (1), entitled *Nitrates from Air*, was delivered on April 9 by E. KILBURN SCOTT, M.I.E.E., A.M.INST.C.E.

#### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

##### ORDINARY MEETING,

Held at the Chemical Society's Rooms, Burlington House, on April 4, Mr. P. A. Ellis Richards, President, in the chair.

Certificates were read for the first time in favour of Mr. Robert C. Grimwood, A.C.G., F.C., D.I.C., A.I.C., and for the second time in favour of Messrs. John Myers, F.I.C., and John Loudon Buchanan, F.I.C.

The following were elected members of the Society: Messrs. Joseph John Valentine Backes, A.R.C.Sc., A.I.C., D.I.C.; Francis Fenelm Donovan, B.Sc. (Lond.); Alfred Edward Johnson, B.Sc. (Lond.), F.I.C., A.R.C.S.I.; Ernest Victor Jones, F.I.C.; S. Gordon Liversedge, F.I.C.; Samuel Gordon Stevenson, A.I.C.; Richard William Sutton, B.Sc.Tech. (Manc.), A.I.C.; Laurence Barnett Timmis, M.Sc. (Tech.) Manc., A.I.C.

The following papers were read:—

*Physiological Standards*, by DR. STANLEY WHITE.

##### Abstract.

Since many important drugs used in medicine do not lend themselves to chemical standardisation it is necessary to adopt physiological standards. A number of individual drugs, including digitalis, ergot and cannabis indica were dealt with, and a method described of arriving at the minimum lethal dose on frogs, and so establishing a heart tonic unit. The standardisation of Pituitrin was discussed, and physiological methods for determining the presence of the three vitamins. The paper was illustrated by numerous slides.

*The Estimation of Boric Acid in "Liquid Eggs" and other Foodstuffs*, by G. W. MONIER-WILLIAMS, M.A., PH.D., F.I.C.

##### Abstract.

The author draws attention to the irregular results sometimes obtained with Thompson's method owing to loss of boric acid by precipitation as calcium borate during the removal of phosphates. A method is described in which phosphoric acid is removed by precipitation as magnesium ammonium phosphate, the subsequent titration of the boric acid being carried out by Thompson's method.

*An Investigation into the Chemistry of the Reinsch Test for Arsenic and Antimony, and its extension to Bismuth*, by B. S. EVANS, M.B.E., M.C., B.Sc., F.I.C.

##### Abstract.

A summary of the literature relating to the reaction is given. A method is described for determining the velocity of the



reaction, and a number of curves are given showing the influence on the reaction velocity of varying chloride, acid strength, or arsenic (antimony, etc.), also the effect of adding cupric or cuprous salts. The products of the reaction are:—

For Arsenic—the compound  $\text{Cu}_3\text{As}_2$ .

For Bismuth—the element Bismuth.

For Antimony—the compound  $\text{Cu}_2\text{Sb}$ , followed by deposition of the element antimony.

In all cases cuprous chloride goes into solution.

An attempt was made to elucidate the mechanism of the reaction, and a number of experiments are described leading to the conclusion that it is due to reduction of the arsenic (or antimony, etc.) by a film of hydrogen on the surface of the copper. Under certain given conditions the test used qualitatively can be made sensitive to less than 0.01 mgrm. per 100 cc.

It is suggested that a determination of the reaction velocity carried out in any doubtful liquid will readily show whether any substance is present which would interfere with the test.

#### THE OPTICAL SOCIETY.

A meeting was held at the Imperial College, Imperial Institute Road, on Thursday, April 12th. The following papers were read and discussed:—

*The Hilger Microscope Interferometer*, by F. TWYMAN, F.INST.P.

*On the Form of the Wave Surface of Refraction*, by A. WHITWELL, M.A.

Mr. J. H. Barton also exhibited a new research microscope of original design.

By the courtesy of Messrs. The Hadley Company, makers of gold-filled spectacle frames and mounts, a visit has been arranged to their works at Portsmouth Road, Surbiton, Surrey, on the afternoon of Thursday, April 26, 1923. Fellows and Members desiring to avail themselves of the privilege of visiting these works should advise the Hon. Secretary (Business) at the Imperial College, not later than Saturday, April 21.

#### THE INSTITUTION OF ELECTRICAL ENGINEERS.

An ordinary meeting was held on Thursday, April 12. A paper entitled *The X-Ray*

*Examination of Materials*, was read by A. G. WARREN, Member.

At the conclusion of the lecture, Mr. E. E. Brooks exhibited some lantern slides illustrating lines of electric force.

#### THE INSTITUTE OF METALS.

A General Meeting of the Institute of Metals will be held at the Institution of Mechanical Engineers Storey's Gate, Westminster S.W.1, on Wednesday May 2, 1923 at 8 p.m. when the thirteenth annual May Lecture will be delivered by DR. W. ROSENHAIN, F.R.S., Vice-President, on *The Inner Structure of Alloys*.

#### IRON AND STEEL INSTITUTE.

The Annual Meeting of the Institute will be held, by kind permission of the Council of the Institution of Civil Engineers, at Great George Street, Westminster, on Thursday and Friday, the 10th and 11th of May, 1923.

#### PROGRAMME OF PROCEEDINGS.

##### Thursday, May 10th.

10 a.m.—General meeting of members. The Council will present their Report for the year 1922. The hon. treasurer will present the statement of accounts for 1922. Scrutineers will be appointed for the examination of voting papers. Election of Council. Presentation of the Bessemer Medal to Dr. W. H. Maw.

A resolution, formal notice of which was given at the autumn meeting, on September 5th, 1922, of the alteration of By-Law 10, relating to the election of the President, will be submitted. The terms of the present by-law are as follows:

"The President shall be elected for two years, and shall not be eligible for re-election until after an interval."

The terms of the resolution are:

"That the By-Law shall be altered as follows: 'The President shall be elected for one year,' and to omit the words: 'and shall not be eligible for re-election until after an interval.'"

A selection of the following papers will be read and discussed in the afternoon session, and also during Friday, May 11:—

C. A. ABLETT, *Economic Principles governing the use of Electrical Power in Iron*

and Steel Works.

J. O. ARNOLD, F.R.S., *On the co-relation of the Chemical Constitutions of "True Steels" to their Micrographic Structures.*

C. R. AUSTIN, *Some Mechanical Properties of a series of Chromium Steels.*

L. E. BENSON and F. C. THOMPSON, *Some Experiments on Grain-growth in Iron and Steel.*

H. C. H. CARPENTER, F.R.S., *The Production of Single Metallic Crystals and some of their properties.*

F. CLEMENTS, *British Steel Works Gas Producer Practice.*

T. P. COLCLOUGH, *The Constitution of Basic Slags—its relation to Furnace Reactions.*

C. H. DESCH and A. T. ROBERTS, *Some Properties of Steels containing Globular Cementite.*

C. A. EDWARDS and C. R. AUSTIN, *A Contribution to the Study of Hardness.*

J. E. FLETCHER, *Some Characteristics of Moulding Sands and their Graphical Representation.*

D. HANSON and J. R. FREEMAN, *The Constitution of the Alloys of Iron and Steel.*

E. J. L. HOLMAN, *Note on a Value for the Surface Tension of Iron Sulphide.*

K. HONDA and T. MURAKAMI, *The Structural Constitution of Iron-Carbon-Silicon Alloys.*

J. J. A. JONES, *The Acl Range in Alloy Steels.*

J. W. LANDON, *Change of Density of Iron due to Overstrain.*

F. C. LANGENBERG, *An Investigation of the behaviour of certain Steels under Impact at different Temperatures.*

T. MATSUSHITA, *Some Investigations on the Quenching of Carbon Steels.*

L. NORTHCOTT, *A Note on Temper Carbon.*

H. O'NEILL, *Variation of Brinell Hardness Number with Testing Load.*

T. F. RUSSELL, *The Potential Energy of Cold Worked Steel.*

J. STEAD, *The Cold Working of Steel with reference to the Tensile Test.*

E. R. SUTCLIFFE and E. C. EVANS, *The Reactivity of Coke as a factor in the Fuel Economy of the Blast Furnace.*

F. C. THOMPSON and A. GOFFEY, *The Changes in Iron and Steel below 400° C.*

J. H. WHITLEY and A. BRAITHWAITE, *Some Observations on the effect of small quantities of Tin in Steel.*

## THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The following paper was read at the Royal Society of Arts on Tuesday, April 10, 1923:—

Potrero No. 4.: *A History of One of Mexico's Earliest and Largest Wells*, by A. E. CHAMBERS, Assoc.M.I.C.E.

Potrero No. 4 is one of the largest producers in Mexico, having given over one hundred million barrels of oil before salt water appeared. Its technical history is little known, and it is in the hope that a detailed description of the life of this well will interest the members that this paper is presented to the Institution.

The career of the well was an eventful one; it was brought in uncontrolled in December, 1910, brought under control in March, 1911, developed large seepage areas in its vicinity early in 1914, caught fire in August of that year, was extinguished early in April, 1915, produced under partial control for nearly four years, until December, 1918, when its production turned to an emulsion, which continued until April, 1919, when the well was finally closed in.

It is situated in the State of Vera Cruz, some 50 kilometres north-west of Tuxpam.

The specific gravity of the crude oil was 0.931° at 60° F., its temperature at the well was 147° F., and the pressure when the well was closed in was found to be 825 lbs. per square inch.

At first, all endeavours were devoted to saving the oil, but it was soon apparent that the quantity being produced was too great to attempt storing it; a careful calculation made in December, 1910, showed that the well was then flowing at the rate of 100,000 barrels in 24 hours. The Buena Vista River, previously mentioned, is the natural drainage for the area where this well is situated, and it was down this stream that immense quantities of oil flowed and were burnt many kilometres away.

It was evident that the only thing to do to save this well and its production, was to bring it under control. Owing to the great pressure and volume of oil, no ordinary method could be used, and several schemes were suggested; finally, however, an appliance, now fairly well known under the name of a "Bell Nipple," was devised and successfully installed in January, 1911.

On August 14, 1914, a severe lightning storm visited the neighbourhood, and set fire to the gas escaping from the well; this gas fire melted some lead gaskets in the joints of the flow line near the well head. The oil from these joints caught fire, also the oil leaking from the bell nipple; the fire rapidly spread to the seepages, and very quickly this large area was completely involved. It was unfortunate that the occurrence coincided with a period of great revolutionary activity and when the American Government had actually advised its nationals to leave Mexico. Practically all the skilled American oilfield workers had therefore left Potrero, leaving operations in charge of a small number of British and other nationalities. These few men were inadequate to deal with the fire in its early stages, and before others could get on the scene, the fire had assumed enormous proportions.

By March 24, 1915, the fire was totally extinguished, and all that remained of the well to be seen was a large earthen mound with numerous gas pipes sticking out from it. After a few weeks the action of the gas on the clays forming the mound had converted them into a loose powdery material, and the gases, instead of coming only from the gas pipes, were exuding from all over the mound. It was thought that this condition of affairs should not be allowed to remain, as, if through lightning or any other cause, the gases became ignited, it was difficult to feel certain that some serious damage might not eventually occur. The whole mound was, therefore, covered with a reinforced concrete cover; the cover being designed by the use of suitable steel frames to be entirely self-supporting, and, in fact, to form a species of inverted cup placed over the earthen mound but not in contact with it. Numerous pipes were inserted in this concrete cap, and the gas coming therefrom was led away and burnt at flares at a safe distance. The well in this condition produced without misadventure until December, 1918.

## SOCIETY OF CHEMICAL INDUSTRY.

### BIRMINGHAM AND MIDLAND SECTION.

The following papers were read at the meeting on March 27:—

### *Oil Hydrogenation*, by E. J. LUSH, M.A.

The physical conditions of the addition of hydrogen to oils, by means of nickel, acting as a catalyst, lent themselves naturally to continuous working. The catalyst being a solid, the oil a liquid, and the substance producing the desired change, viz., hydrogen, a gas, it should be possible to distribute nickel throughout a closed vessel, keep the vessel full of hydrogen, and allow oil to run in at one end and out at the other—the speed of flow regulating the degree of hydrogenation.

### *Reaction between Ammonia and Sodium Hypobromite*, by D. R. NANJI, M.Sc., and W. F. SHAW, M.Sc.

When ammonia is added to excess of alkaline sodium hypobromite, it is decomposed. That this reaction is not the only one that occurs has not been recognised by certain investigators since it has been suggested as the basis of volumetric estimations of ammonia. Ammonia is decomposed by adding it to excess of sodium hypobromite, the excess of the latter being determined after addition of potassium iodide, by titrating the liberated iodine with thiosulphate.

The authors' results prove that this basis is not sufficiently accurate.

### *The Estimation of Acetone and of Ethyl Alcohol in a mixture of the two*, by J. H. BUSHILL, B.Sc.

The object was to estimate these substances in comparatively small quantities in the products of fermentation by various bacteria. The method of estimating acetone by Rakskit was preferred to others. The method used by Northrop and his co-workers for estimating alcohol by oxidising with potassium dichromate and sulphuric acid was criticised. The author prefers to estimate the specific gravity of the mixture which, together with the acetone content, gives the alcohol present. For this, acetone gravity tables up to 1 per cent. had to be constructed.

A known volume was made slightly alkaline with soda and distilled, the distillate being made to a definite volume. The gravity of this solution is then taken and

the acetone estimated. By means of the acetone tables the gravity of the acetone present can be found, and from this and the gravity of the mixture the alcohol may be estimated.

#### HYDROHEPATOSIS, A CONDITION ANALOGOUS TO HYDRONEPHROSIS.

BY PHILIP D. McMASTER AND PEYTON ROUS.

*Rockefeller Institute of Medical Research,  
New York.*

*Read before the Academy, Nov. 15, 1922.*

The changes which follow obstruction to the common bile duct in human beings are highly various; and clinical and autopsy records yield few clues to the factors responsible for this diversity. We have attempted to come at them by animal experiment.

The fluid found in the distended ducts above an obstruction that has endured some time may be heavily loaded with bile pigment and mucus, green-black and tarry, or so wholly devoid of these constituents, despite a pronounced jaundice of the tissues in general, that it is colourless, limpid and watery. All gradations between such extremes are met with. We have shown in previous papers<sup>1,2</sup> that in the absence of infection all are traceable to the differing influences of the gall-bladder and ducts upon the bile first pent in the channels. The ducts elaborate a secretion of their own, which, thin and colourless, tends gradually to replace the bile; whereas the gall-bladder, by virtue of special abilities to concentrate the bile<sup>2</sup> and add mucus thereto, acts to fill the passages with one so thick and inspissated that the secretion just mentioned dilutes it but slowly and never replaces it perfectly. When the gall-bladder fails to exert its characteristic influences, as happens sometimes after injury to the organ, the fluid collecting in it, and in the ducts as well, is a colourless "white bile" similar to that contained in obstructed ducts unconnected with the *receptaculum felleæ*.

These are the findings after total obstruction. The changes taking place when the liver continues to secrete into the proper channels but against a pressure obstacle, have not only theoretical interest but a practical one as bearing upon the development of gallstones. We have

studied them with the aid of a method whereby in dogs the common duct, and very probably the duct of any gland lying within the peritoneal cavity, may be permanently intubated and the secretion collected. The method depends upon the ability of the omentum to limit the spread of infection. When a rubber tube is connected with an intraperitoneal duct and led directly through the abdominal wall, it ordinarily comes away within a few days as the result of an ascending purulence. But if the tube be so bent upon itself that a considerable stretch of it, sheathed in omentum, is interposed between the duct and the exit wound, infection does not travel along it and it remains permanently in place. The pressure obstacle necessary to the observations was found, in some instances, in the tissue adhesions that developed about a balloon for bile collection which was interpolated in that part of the tube system lying within the abdomen. As the adhesions gradually thickened and contracted, they brought to bear an increasing resistance to the expansion of the balloon. In other instances, in which the balloon was placed outside of the animal in a basket moored to the skin, small gallstones forming in the lumen of the glass canula placed in the common duct interfered as they enlarged with the passage of the bile. Whichever the type of obstacle the same series of changes in the bile took place. From day to day, as the pressure against which the fluid was secreted became greater, it gradually lost the characters distinguishing it as bile. While still fairly copious, it contained less and less bilirubin, cholesterolin and bile salts. Only faint traces of these substances were present in the last scanty specimens obtained before obstruction became complete. The final fluid distending the ducts was a "white bile" such as has already been mentioned, that is to say, no bile at all, in the ordinary sense of the term.

A comparison of the liver changes with those occurring in other glands after duct obstruction has proved enlightening. These changes have been best studied in the kidney. In this organ the pressure under which the retained secretion is held interferes with the venous flow—and it does this in the liver as well, a point which we have brought out in a previous paper.<sup>3</sup> Both organs continue to secrete; but the secretion is now turned back into the body. There is in both a progressive connective

tissue proliferation, and an accompanying parenchymal atrophy. The atrophy may become complete when only one kidney is affected; but when the outflow of urine from all of the renal tissue is interfered with death ensues long before the alterations progress so far. Similarly, obstruction of the bile ducts from but a portion of the liver leads to a complete parenchymal atrophy in the region concerned<sup>4</sup>; whereas if the common duct, which drains all of the organ, be occluded, the individual dies at a time when the hepatic changes are still relatively slight.

A striking early change in the kidney is sacculation, and the sac may come to contain several litres of a watery fluid devoid of the characters of urine—hence the name for the condition, *hydronephrosis*. Obstruction of the duct from the liver leads to a marked distention of the bile channels, but the organ itself does not bag out, a difference scarcely surprising when one considers that the maximum pressure developed upon biliary obstruction is extremely low (350 mm. of the bile itself, in the dog), whereas on renal obstruction it is high (from 650 to 900 mm., in terms of bile). The fact that the fluid ultimately found in the distended ducts from the liver has, in the absence of gall-bladder influence, none of the characters of bile, has been sufficiently indicated. When secretion takes place against a pressure obstacle there is a reduction both in the total output and in the percentage output of some substances, exactly as with the kidney.<sup>5</sup> Whether, as in the case of the latter organ, the percentage output of certain other substances is increased, remains to be determined.

From this comparison it will be seen that the changes consequent upon biliary obstruction and upon renal obstruction, respectively, are essentially similar in type. They are indeed the changes which follow obstruction to the ducts of glands in general; and the differences between the renal and hepatic manifestations of them are traceable merely to incidental peculiarities of the glands concerned. These facts would long ago have been recognised, were it not for the complicating activities during biliary obstruction of an extraneous organ, the gall-bladder. As indicating the essential likeness of the hepatic to the renal changes, we would suggest that the term *hydrohepatosis*

be applied to the condition found after obstruction to the outflow of bile. When the contents of the obstructed ducts have been altered through the gall-bladder activity, the hydrohepatosis is *concealed*, in a very real sense; but when this has not happened, and the distended ducts are in consequence filled with "white bile," there is a *manifest hydrohepatosis*. But the terms have little importance as compared with the understanding that they are supposed to convey.

<sup>1</sup> Rous, P., and McMaster, P. D., *J. Exper. Med.*, Baltimore, 1921, XXXIV., 47.

<sup>2</sup> Rous, P., and McMaster, P. D., *Ibid.*, 1921, XXXIV., 75.

<sup>3</sup> Rous, P., and Larimore, L. D., *ibid.*, 1920, XXXII., 249.

<sup>4</sup> Nasse, *Verhandl. deutsch. Ges. Chir.*, 1894, Berlin, XXIII., Pt. 2, 525.

<sup>5</sup> Cushny, A. R., *The Secretion of the Urine*, London, New York, Bombay, Calcutta, and Madras, 1917.

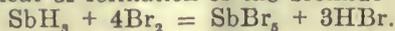
[Reprinted from the *Proceedings of the Academy of Sciences of the U.S.A.*]

## CORRESPONDENCE.

### THE HEAT OF FORMATION OF STIBINE.

To the Editor of THE CHEMICAL NEWS.

SIR,—I would like to point out that in nearly all the English textbooks on chemistry the heat of formation of stibine for one molecule is given as -84.5 calories. This value was found by Berthelot and Petit (*compt. rend.*, 1889, CVIII., 546-550) from the heat of formation of the bromide



In 1908, however, A. Stock and W. Wrede (*Ber.*, 1908, XLI., 540-543) found the heat of formation of stibine by decomposing the gas quantitatively into its elements by an electric spark. The value they obtained for one molecule was -34 cal.

This latter paper appears to have been little noticed by English authors, for we find J. Thomlinson (*The Chemical News*, 1909, XCIX., 133) assuming the earlier value. His results are valueless in the light of the experiments of A. Stock and W. Wrede.

In most of the German textbooks on chemistry, the value -34 cal. is now taken instead of the previous one of -84.5 cal.—Yours, &c.,

EDWARD J. WEEKS, B.Sc., F.C.S.  
The Sir John Cass Institute.  
April 4, 1923.

#### NOTICES OF BOOKS.

*Oxidations and Reductions in the Animal Body*, by H. D. DAKIN, D.Sc., F.I.C., F.R.S. Second edition. Longmans, Green & Co., London. 1922. 6s. net.

It is eleven years since the first edition of this monograph appeared, and during this period much progress has been made in unravelling the mechanism of the various reactions which occur in the animal body. This advance has been general rather than specific, and accordingly the arrangement of the subject matter follows very closely that of the first edition, and it is only in dealing with the biochemistry of the carbohydrates that considerable alterations have been rendered necessary in order to incorporate the results of recent investigations. This monograph is devoted to the consideration of oxidation and reduction processes of the animal body, from the standpoint of the structure of the substances undergoing change. The purely biological aspects and also the thermo dynamics of the problems of oxidation and reduction have been omitted as being outside the scope of the work. The necessity for this intensive study of intermediary metabolism is justified owing to the developing appreciation of the fact that different proteins, fats, and sugars are not physiologically equivalent, and that certain definite chemical groups subservise special functions in the animal organism.

As the author points out, the oxidations and reductions occurring in the living body are so closely interwoven with other types of reaction, especially those involving condensation and hydrolysis, that their consideration, apart from other metabolic changes, is becoming unduly artificial, and will probably be abandoned in the near future. If this turns out to be so, we trust that the author will be chosen to give us that more extensive view of metabolic changes when the time arrives. The only blemish to be found in this monograph is

the presence of a large number of small errors due to faulty proof reading and carelessness in setting up the type.

An excellent bibliography, and an index complete a book which we have no hesitation in recommending to all interested in biochemistry.

*Vital Factors of Foods—Vitamins and Nutrition*, by CARLETON ELLIS, S.B., F.C.S., and ANNIE L. MACLEOD, Ph.D. Pp. XVII. + 391. London: Chapman & Hall, Ltd., 11, Henrietta St., W.C.2. 1923. Price 25s.

Not so many years ago it was believed that a balanced diet should contain protein, fat, carbohydrates, and certain salts in correct proportions, and then the animal body would continue to thrive. Great importance was attached to the calorie or energy value of foods.

To these, investigations of the past decade have added the essential inclusion of accessory food factors or vitamins.

It is, perhaps, surprising that substances which play so vital a rôle in nutrition should have escaped discovery for so long, but it is now definitely established at least three accessory factors are necessary, viz., the fat-soluble, growth-promoting Vitamin A, the water-soluble, anti-neuritic Vitamin B, and the anti-scorbutic Vitamin C. (Continued investigations may lead to the definite characterisation of a fourth.)

It has come to be realised that a number of maladies are not caused by the presence of toxins, as previously supposed, but by the absence of vitamins.

The authors have given a careful account of the discovery of the existence of these three vitamins and their specific functions. They have also indicated the different requirements of these in the food of children and adults.

Little is known at present concerning the chemical properties of the vitamins, and still less of their structure. The attempts of Funk and others to isolate pure vitamin are recorded. In this and other connections the original literature has been quoted and searched very thoroughly, so that all existing knowledge on the subject has been ably summarised.

Very few errors have been noted, but references are not quoted uniformly. This very minor defect will, doubtless, be re-

moved in the next edition, which should not be long in appearing.

In their comprehensive treatise the authors have dealt with the subject authoritatively in a lucid manner which cause the book to appeal to the general public as well as to scientists.

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*The Generation and Utilisation of Cold.* A general discussion held by the Faraday Society. Pp. 136. London: The Faraday Society, 10, Essex Street, W.C. 1923. Price 10s. 6d.

From time to time the Faraday Society holds discussions upon physico-chemical subjects of both scientific and industrial interest. These deliberations are printed in the *Transactions* of the Society, but in order to give them a wider publicity the Society also issues them in the form of *Reprints*.

The present volume is an account of a general discussion on the Generation and Utilisation of Cold, which was held jointly by the Faraday Society and the British Cold Storage and Ice Association last October.

Part I. deals with the laboratory methods of Liquefaction. Prof. H. Kammerlingh Onnes has contributed an article on the lowest temperature yet obtained, and an account of the apparatus and methods adopted to attain low temperatures in the Leiden Cryogenic Laboratory is given by Dr. C. A. Crommelin; both contributions are fully illustrated. This, the more academical, portion concludes with a short paper on Ethyl Chloride, by Prof. C. F. Jenkins, and an account of the discussion on the laboratory methods of liquefaction in which a number of eminent authorities participated.

Part II. contains the contributions on the Industrial Methods of Liquefaction and the practical applications of low temperatures. After a general survey by K. S. Murray, follow papers by M. Georges Claude, E. A. Griffiths, A. J. Bremner, Dr. E. Griffiths and J. H. Aubery, and Cosmo Jones. All these contributions deal with some special aspect of technical importance.

The industrial importance of the achievements in this field can scarcely be over-estimated.

*Laboratory Manual of Physical Chemistry*, by ALBERT W. DAVISON and HENRY S. VAN KLOOSTER. Pp. VIII. + 182. London: Chapman & Hall, Ltd., Henrietta Street, W.C. 1922. Price 10s.

Lecturers in physical chemistry and laboratory demonstrators should find this manual both useful as a guide and helpful to indicate to students the exact apparatus needed for a given experiment and the method of arranging it.

In practical physical chemistry this is an advantage since it is seldom possible for all students to commence simultaneously with the same experiments.

Each experiment is set out in a clear and concise manner. The *object* is first stated, *references* are then quoted, frequently in three categories—textbooks, laboratory manuals and original articles. A list of *apparatus and chemicals required* comes next, and is followed by the *method of procedure*. There is then a blank scheme with instructions for entering *observations and measurements*. Finally the *calculations* required are indicated. Blank sheets and graph paper have been introduced, so that the manual can also serve firstly as a notebook and later as a reference volume.

As regards the experiments selected, these follow the usual lines, except that the procedures have been modified in many cases. Some of the methods have not appeared previously in textbooks.

Students who complete those described cannot fail to obtain a good general acquaintance with practical physical chemistry.

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Messrs. The Eastman Kodak Company, of Rochester, N.Y., have forwarded us their fifth volume of *Abridged Scientific Publications*—now being published annually.

The 172 pp. have been filled with various papers compiled from research-records of the Kodak Laboratories, which were published in a wide range of scientific periodicals during the year 1921.

From the collection, one may judge that the science of photography will develop enormously during the next few years. L. Silberstein has included a most interesting paper upon the propagation of light in rotating systems, and S. E. Sheppard (very much in evidence throughout the volume)

criticises Mr. Renwick's theory that "it is . . . silver which first undergoes change on exposure to light" in discussing the contention that the highly dispersed silver halide is converted into a more condensed one.

It is to be regretted that various formulæ have been omitted from L. A. Sones' and C. E. Fawkes' paper upon the *Reduction of Developing-out Papers*, as the arguments and observations seem incomplete without them. Also, the experimental apparatus described on p. 75 seems a trifle vague, and could well do with more explanatory illustration than that on p. 81.

However, the work is admirably edited and printed. Perhaps, to render it more complete, the entire papers could well have been inserted, instead of congests; and their sources kept free of the matter by including them in the contents-table.

#### BOOKS RECEIVED.

*Atomic Theories*, by F. H. LORING. Pp. X. + 218. Second edition, revised. 1923. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C.2. 12s. 6d. net.

*Elements of Glass-Blowing*, by H. P. WARAN, M.A., PH.D. Pp. VIII. + 113. 1923. Messrs. G. Bell & Sons, Ltd., York House, Portugal Street, W.C.2. 2s. 4d. net.

*Wavelength Tables for Spectrum Analysis*, by F. TWYMAN, F.INST.P. Pp. VIII. + 106. 1923. Messrs. Adam Hilger, Ltd., 75a, Camden Road, N.W.1. 7s. 6d. net.

Bulletins issued by the U.S. Department of the Interior, Bureau of Mines:—

No. 218: *The Technology of Slate*, by OLIVER BOWLES. Pp. 132. Price 20 cents.

No. 201: *Prospecting and Testing for Oil and Gas*, by R. E. COLLOM. Pp. 170. Price 25 cents.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

7505—Coley, H. E.—Manufacture of barium sulphide and hydroxide. March 15.

7473—Spence, H.—Preparation of titanium compounds. March 15.

7407—Waterloo Chemical Works, Ltd.—Manufacture of ferric hydroxide. March 14. *Specifications Published this Week.*

193881—Hybinette, N. V.—Separating, plating and refining of metals by electrolysis.

193894—Compagnie Francaise Thomson-Houston.—Production of boron and boron oxide for use in purifying copper castings.

171094—Pollak, Dr. F.—Manufacture of condensation products from formaldehyde and urea, thiourea, or their derivatives.

193912—British Cellulose & Chemical Manufacturing Co., Ltd., and Bader, W.—Treatment of cellulose acetate products.

193934—Accioly, F. De M.—Treatment of mineral and other oils for the production of volatile liquids adapted for use as fuel.

193967—Hailwood, E. A.—Annealing lehr.

#### Abstract Published this Week.

192298—Alkaloids—Boehringer Sohn, C. H., and Stenzi, H., Nieder-Jngelheim-on-Rhine, Germanp.

*Papaverine nitrite* is prepared by the action of salts of nitrous acid on soluble salts of papaverine; the product is freed from papaverine by means of solvents such as benzene, toluene, tetrahydronaphthalene, or alcohol. The reaction may also be effected in the presence of one of the above mentioned solvents, examples of each method being given. The product exhibits the tissue dilating properties of its components in an enhanced degree.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3288.

## CANADIAN CHEMICAL SUPPLIES.

### THE EXPLOITATION OF CAPITAL.

Mineral secretions in the prairie districts have not, in the past, been regarded as sufficiently extensive to warrant the attention of industrial enterprise. Dr. Charles Camshell, deputy minister of mines, and Dr. A. W. G. Wilson, chief engineer of the mineral resources division, have now issued a report showing the activity in producing chemicals from the alkali deposits of Manitoba, Saskatchewan, Alberta, and British Columbia.

A few details showing the progress might be of interest. A plant costing \$500,000.00 has been constructed at Dana, Sask. (the property of the Salts and Chemicals, Ltd.), and is operating upon the brines of the Muskiki Lake, 23 miles west of Humboldt. The estimated output of the plant is 30,000 tons of salt cake per annum, in addition to Epsom and other salts. The Bishopric and Lent Co. have founded a working at Frederick Lake, five miles south-west of Dunkirk, Sask. It is hoped, at a very early date, to produce 200 tons per day of salt cake; its present output being about 50 tons. An experimental plant has been devised for the Soda Deposits, Ltd., at Fusilier, Sask.; here exists a very pure deposit of sodium sulphate, some of which has already been shipped.

Other companies which are exploiting these districts are:—The Basque Chemical Co., at a lake 15 miles west of Ashcroft, B.C., for crude magnesium sulphate; and the Lillooet Soda Co., at a place 50 miles north of Clinton, B.C., for sodium carbonate.

Quoting from *Natural Resources*, published by the Department of the Interior, Ottawa: "The operations of these companies tend to bring before the public the possibilities of the western provinces in the mineral field, and should form the nucleus of the ever-increasing industry which, in time, should prove of great importance to the whole of Canada."

The Mines Branch of the Department of Mines, Ottawa, have organised a thorough investigation into the localities and extent of the unworked deposits, mainly for Glauber's salt, salt cake, Epsom salt, soda ash, and baking sodas. The secretions are

believed to contain profitable amounts of magnesium salts, and acid sodium carbonate. The investigations are in charge of Mr. S. H. Cole, of the Department of Mines. J.M.

## THE PROBLEM OF SUBSTITUTION IN THE BENZENE NUCLEUS AND THE THOMSON-LEWIS-LANGMUIR THEORY OF CO-VALENCE.

BY RONALD FRASER AND JAMES ERNEST HUMPHRIES.

The work of the organic chemists who have directed their attention to the problem of substitution in the benzene nucleus falls naturally under two heads: speculation on the mechanism of substitution and the study of the directive influence of substituents already present in the nucleus. The present paper deals only with the second part of the problem, though it is realised that the two are probably interdependent, and the possible effect of addition preceding substitution has been kept constantly in view.

Modern theories, as exemplified by the ideas of Lapworth, Fry, Vorländer, Prins, and Flürscheim,\* agree in regarding orientation as occasioned by a differentiated condition—polarity or state of strain—of alternate carbon atoms. These theories inevitably bear among themselves a certain formal analogy, and the ideas here developed are no exception. They agree more particularly with those of Lapworth and Fry in possessing an electrical basis. Nothing is postulated, however, as to the constitution of the benzene nucleus, except that it is, of course, regarded as a six-membered ring; and we consider that the state of the molecule after the entry of a substituent and resulting from its pre-

\* The following references may be given to the papers of these authors: Lapworth, *Mem. Man. Phil. Soc.*, 1920, LXIV., ii., 1; *T.*, 1922, CXXI., 416; Fry, *The Electronic Conception of Valence and the Constitution of Benzene*, 1921; Vorländer, *Ber.*, 1919, LII. (B), 263; Prins, *Chem. Weekblad*, 1918, XV., 571; Flürscheim, *J. pr. Chem.*, 1902, LXVI., 321; *ibid.*, 1905, LXXI., 497.

sence is the important factor in orientation (*cf.*, Mills, *J. Soc. Chem. Ind.*, 1921, XL., 417, R., in his review of Fry's monograph).

We have taken as our basis the Thomson-Lewis-Langmuir theory of co-valence, and on this foundation have built up an electronic interpretation of Lapworth's Principle of Induced Alternate Polarities, as already elaborated by Kermack and Robinson (*T.*, 1922, CXXI., 427). We are not prepared at the present stage to differentiate between the relative sizes of the octets surrounding positive and negative centres, and for our present purpose this appears to be of secondary importance. The development of the theory is based on the following three postulates. In order to avoid the introduction of unnecessary synonyms, we shall adopt in the sequel the terminology used by Kermack and Robinson (*loc. cit.*).

*Postulate 1:* The tendency of a disintegrated octet is towards further disruption; and of a nearly completed octet towards completion.

*Postulate 2:* The tendency towards octet stability of an atom with nearly completed octet is greater than the tendency to octet instability of an atom with disruption only incipient.

*Postulate 3:* The more nearly a group approaches octet stability, the greater the ease of replacement at that point.

It will be observed that Postulate 2 is simply a statement in terms of octets of the conclusion arrived at by Briggs (*T.*, 1908, XCIII., 1564; *ibid.*, 1917, CXI., 253; *ibid.*, 1919, CXV., 278), viz., that negative fields are in general stronger than positive fields. Further, the relation of the carbon atom to Postulate 2 is of importance. It is generally recognised that carbon is unique in that it occupies the middle position in the first series of the periodic system, and is the first member of its group, containing the fewest number of electrons. It follows, then, that in a chain of carbon atoms of alternately positive and negative character, the positive centres tend to increasing positive character, and the negative centres to increasing negative character. Some interesting consequences of this element's electrical individuality will appear in the sequel.

Postulate 3 requires further discussion. We are of opinion that the distinction between polar and non-polar compounds is merely one of degree, and our views in this

respect are those of Briggs (*T.*, 1921, CXIX., 1879), and of Kermack and Robinson (*loc. cit.*). The extreme case of octet stability is evinced in compounds which have come to be known as polar, where an atom surrounded by a completed octet can actually exist free as an ion (*e.g.*, sodium chloride). There are evidently all gradations of octet stability from such extreme cases to those of typically non-polar compounds such as carbon dioxide, where octet stability is apparently only possible so long as there is electron-sharing among the octets. It is practically a universal rule that the reactivity of compounds, as measured by the velocity of reaction, is greater in the case of ionised than of non-ionised bodies, although some doubt is thrown on the complete generality of this statement by the work of Kahlenberg (*J. Phys. Chem.*, 1902, VI., 1; and subsequent papers. Compare, however, Stieglitz's discussion of Kahlenberg's results, *Qualitative Chemical Analysis*, Part 1., 1912, pp. 84-87). Thus, although we do not anticipate ionisation as a cause of the reactivity of a substituent possessing a stable octet, we do, as a result of the consideration of the above gradation in reactivity, regard increasing octet stability as parallel with increasing likelihood of lability.

#### THE BROWN AND GIBSON RULE.

Of the many empirical rules which have been from time to time proposed to summarise the directive influence of substituents on an entering group, undoubtedly the best known is that of Brown and Gibson (*T.*, 1892, LXI., 367). It was unfortunate that Brown and Gibson based at least part of their rule on the lack of knowledge of certain reactions (*cf.*, Holleman, *Bull. Soc. Chim.*, 1911, IV., series 9, 1-14). Brown and Gibson based their rule on the oxidisability or otherwise of the compound HX, where X is the substituent, whereas the real basis of the rule is rather the tendency to oxidation or reduction of the substituent itself. On the electronic theory of oxidation and reduction, oxidation means loss of electrons, reduction gain of electrons. The ortho-para directive substituents listed by Brown and Gibson have in each case the atom which is linked to the nucleus in a state approaching octet stability, hence loss of electrons (*i.e.*, oxidation) is resisted (Postulate 1); while in the

case of the meta-directive substituents, viz.,  $\text{NO}_2$ ,  $\text{COOH}$ ,  $\text{SO}_3\text{H}$ ,  $\text{COCH}_3$ , the octets of N, C, S, C, are in a state of incipient disruption due to the effect of the negative (octet stable) O,  $\begin{array}{c} \text{O} \\ \vdots \\ \text{O} \end{array}$ ,  $\text{O}_3$ ,  $\text{OCH}_3$  respectively (cf., Kermack and Robinson, *loc. cit.*): hence loss of electrons (i.e., oxidation) is favoured (Postulate 1).\*

In short, *negative (octet stable) substi-*



Fig. 1.

\*  $\text{CCl}_3$  is listed by Brown and Gibson among the ortho-para directive substituents, by Vorländer (*loc. cit.*) among the meta-directive substituents. Spreckels (Ber., 1919, LII., B, 315) has obtained the meta nitro compound under conditions which preclude hydrolysis. This is in complete agreement with the octet view, for the carbon atom in  $\text{CCl}_3$ , being attached to three negative (octet-stable) chlorines, is a positive centre, and hence falls into the meta-directive class. Cf., also below.

It is convenient to note here the meta-directive nature of the ammonium salt group, as investigated by Vorländer and Siebert (Ber., 1919, LII. [B], 233). On nitrating  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{NO}_3$ , for instance, the meta compound is obtained. It is evident that the condition of octet stability in

$\begin{array}{c} + \quad - \quad + \\ \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_3\text{NO}_3 \end{array}$  is as shown, the signs + and - indicating polarity as resulting from octet instability and octet stability respectively; the N atom attached to the nucleus being a positive centre, the whole group would be expected to direct meta.

We might mention here that some of the ortho-para directive substituents, comprised of a side chain (Vorländer, *loc. cit.*), present a difficulty inasmuch as the induced polarity of the nucleus would appear to differ from case to case, as, for example, in  $\cdot\text{CH}_2\text{COOH}$ ,  $\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$ ,  $\cdot\text{CH}\cdot\text{CH}\cdot\text{COOH}$ , all these groups, however, being ortho-para directive.

*tients direct ortho-para; positive (octet unstable) substituents meta.*†

From the above argument the state of polarity of the carbon atoms in a mono-substituted benzene compound containing (1) an ortho-para directive substituent X (Fig. 1, a), and (2) a meta directive substituent Y (Fig. 1, b) readily follows. In Fig. 1, a, the octet of X tends to completion; hence the electrons shared with  $\text{C}_1$  are drawn into X, making  $\text{C}_1$  positive;  $\text{C}_2$  can now appropriate electrons shared with the unstable system  $\text{C}_1$ , acquiring negative polarity;  $\text{C}_3$  assumes positive polarity, and so on. In Fig. 1, b, containing Y in a state of incipient disruption, the polarities are obviously as shown (cf., Lapworth, *Mem. Man. Phil. Soc.*, 1920, LXIV., ii, 1).

A consideration of the figures will show that whatever is the cause of ortho-para substitution in Fig. 1, a, will cause meta substitution in Fig. 1, b. The elucidation of these causes involves a special consideration of the position of hydrogen with regard to octet stability. We regard the condition corresponding to octet stability of hydrogen as represented by the nucleus with no electrons.\* On this view, the hydrogen atom should be almost entirely lacking in a tendency to acquire an electron, and become the negative hydrogen postulated by Fry (*op. cit.*, pp. 20-27, p. 50). Our views receive strong support from the arguments of Stieglitz (*J. Amer. Chem. Soc.*, 1922, XLIV., 1293) against the existence of negative hydrogen in benzene compounds.

† Attention should be directed at this point to the use of the terms positive and negative applied to the groups mentioned, in view of the fact that in discussions on orientation the terms are used, arbitrarily and in general, with the opposite meaning. This has already been noticed by Davies (T., 1922, CXXI., footnote to p. 786). The same writer (T., 1922, CXXI., 809) disproves the statement made by one of us (Fraser, T., 1922, CXXI., 195) that the directive influence of substituents was partly dependent on their volume.. The statement above is now preferred.

\* These remarks bring hydrogen (and the metals) into line with Postulate 2, which was stated in such a form as to make more obvious its application to the common organic elements, which lie to the right of the Periodic Table.

The main consideration seems to be rather the state of the carbon atom to which the hydrogen is attached. In a carbon atom of negative polarity, the octet is comparatively firmly held; hence the hydrogen attached to it is to a great extent deprived of its electron; the converse holding with a carbon atom of positive polarity. Bearing in mind the unique position of hydrogen with regard to octet stability, it is evident that the hydrogen nuclei attached to negative carbon atoms are in a condition for ready substitution (Postulate 3).

Thus it is evident (Fig. 1) that the ortho-para hydrogens in Fig. 1, a, are in a condition for ready substitution, while in (b) it is the meta hydrogens which are the more easily replaced. It is seen that the essential difference between the two types of substitution is brought out with exceptional clearness on this view; and, further, the ortho-para directive influence of X on the one hand, and the meta-directive influence of Y on the other, is as it should be, independent of the nature of the entering group.

The special reactivity of the hydrogen in the para-position to an ortho-para directive substituent follows immediately from the above considerations, inasmuch as (Fig. 1, a), there is a reinforcing negative influence on the polarity of the 4-carbon atom.

#### ENTRY OF POSITIVE GROUPS.

It is well known that most of the radicles which can be introduced directly (*i.e.*, without the action of catalysts), into the benzene nucleus are positive (octet unstable). This follows at once from the preceding considerations. We have computed the number of electrons present in the typical positive radicles, COOH, SO<sub>3</sub>H, and NO<sub>2</sub>, with the following results: (1) COOH, charge + 1, has sixteen electrons available for the formation of octets; adopting the Hantzsch-Lapworth structure for carboxyl, it is found that the carbon atom contains only six electrons in the sheath,

thus:  $\text{C} \begin{array}{c} \cdot\cdot\cdot\text{O} \\ \cdot\cdot\cdot \\ \cdot\cdot\cdot\text{O} \\ \cdot\cdot\cdot\text{H} \end{array}$ . If the group replace a

hydrogen nucleus, the carboxyl carbon can readily complete its octet by sharing with the negative (octet stable) carbon atom in the nucleus, the octet of this atom being left complete by the removal of the hydrogen nucleus. (2) SO<sub>3</sub>H. In sulphonation

H<sub>2</sub>SO<sub>4</sub> reacts as OH<sup>-</sup> and SO<sub>3</sub>H<sup>+</sup>; on this basis, the SO<sub>3</sub>H radicle contains twenty-four electrons available for octet formation.

This leads to the structure  $\text{H}:\ddot{\text{O}}:\text{S} \begin{array}{c} \cdot\cdot\cdot\text{O} \\ \cdot\cdot\cdot \\ \cdot\cdot\cdot\text{O} \end{array}$

in which the sulphur atom contains only six electrons in the sheath. (3) NO<sub>2</sub>. In nitration, HNO<sub>3</sub> reacts as OH<sup>-</sup> and NO<sub>2</sub><sup>+</sup>; on this basis the number of electrons in the NO<sub>2</sub> radicle available for octet formation is

eighteen; this leads to the structure  $:\text{N} \begin{array}{c} \cdot\cdot\cdot\text{O} \\ \cdot\cdot\cdot \\ \cdot\cdot\cdot\text{O} \end{array}$

in which the unstable centre, N, again con-

tains six electrons in the sheath. Similar arguments regarding the replacement of hydrogen apply to cases (2) and (3) as hold in (1).

It is clear that a negative (octet stable) substituent will not possess an electron content able to give the easy attainment of octet formation such as is possible in the cases cited above for positive substituents, and hence we should not expect the negative class to be so readily susceptible to direct introduction into the nucleus.

It is possible that we have here an underlying reason for the greater stability of compounds of the type (b) (see Fig. 1) than those of type (a) (*Cf.* Vorlander, *loc. cit.*).

#### THE HOLLEMAN SERIES.

The relation between octet stability and directive influence can now be discussed. Consider a typical case of a di-substituted derivative, C<sub>6</sub>H<sub>4</sub>XY, where the octet stability of X is greater than that of Y.

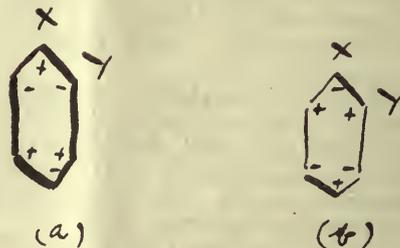


Fig. 2.

It follows from the relative stabilities of the octets of X and Y that the polarities of the carbon atoms should be as illustrated in Fig. 2 (a) rather than that shown in

2 (b). Generalising, it can be stated that the relative directive power of substituents follows a descending order of octet stability, and this seems to us to be the real implication of the Holleman series.

Holleman (*Die direkte Einföhrung von Substituenten in den Benzolkern*, 1910, 466-469) points out that the directive tendencies of the commoner substituents follow the descending order: OH, NH<sub>2</sub>, Cl, I, Br, CH<sub>3</sub>, COOH, SO<sub>3</sub>H, NO<sub>2</sub>. The tendency to octet stability doubtless follows the descending order: O > N > C (*cf.* Briggs, *Phil. Mag.*, 1921, vi., XLII., 449-450); this accounts for the position of OH, NH<sub>2</sub>, CH<sub>3</sub>, it being remembered that the kernel octets are attached to positive hydrogen nuclei. The greater volumes of Cl, Br, I, agree with their comparatively low place in the series, increase in electropositiveness with increase in volume being a well established tendency which is readily interpreted electrically.\* One would expect fluorine to be above hydroxyl in the series (see below). That all ortho-para directive substituents precede the meta follows from Postulate 2. Considering the meta-directive substituents among themselves, it is evident that electrons are more easily drawn from the labile carbon atom than from the more electropositive sulphur. The larger volume of sulphur as compared with nitrogen agrees with its high position, the effect of electropositiveness being here

opposite to that obtaining in the ortho-para directive series.

All possible cases of the entry of the third group into a disubstituted derivative will now be considered.

In the disubstituted compounds represented above, X<sub>1</sub> and X<sub>2</sub> are ortho-para directive (octet stable) substituents; Y<sub>1</sub> and Y<sub>2</sub> are meta directive (octet unstable) substituents.

Case 1: Fig. 3, i. The induced polarities of the carbon atoms is as shown in (a) and (b), according as the influence of X<sub>1</sub> or X<sub>2</sub> predominates. Since the inductive effects are opposed, there will be an equilibrium between the two electromers, as indicated above.

(To be Continued.)

\* The position of iodine relative to chlorine and bromine offers a curious anomaly. Owing to the differences of opinion existing with regard to the arrangement of electrons in the heavier atoms (Bohr, *NATURE*, 1921, CVII., 104; Bury, *J.A.C.S.*, 1921, XLIII., 1602), we have not attempted to account for it.

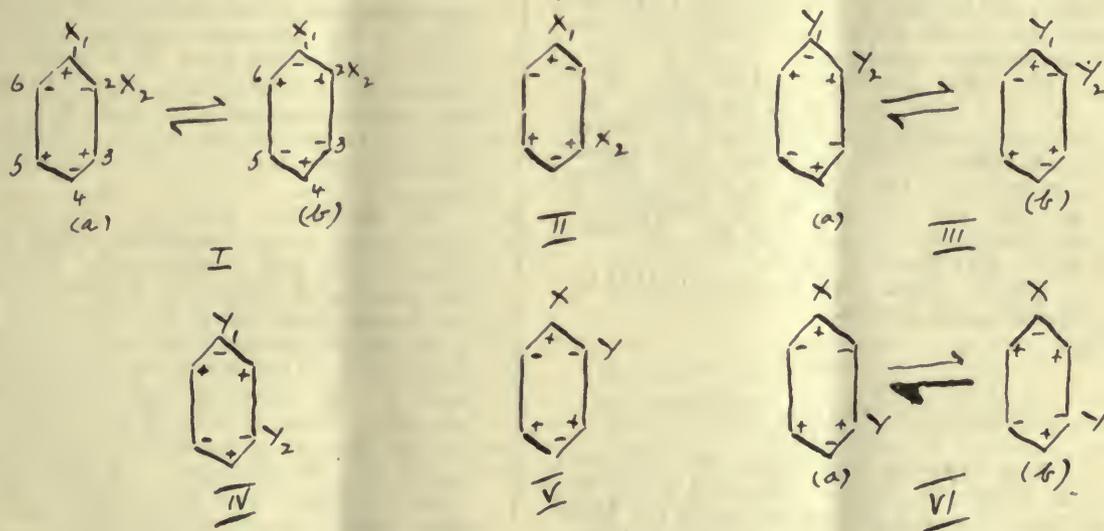


Fig. 3.

### INTERVIEW WITH COMMERCIAL SECRETARY ON TRADE WITH POLAND.

Mr. R. E. Kimens, C.M.G., Commercial Secretary to His Majesty's Legation at Warsaw will be in attendance at the Department of Overseas Trade for one week, commencing on April 18. During that period he is prepared to interview by appointment United Kingdom manufacturers and merchants interested in trade with Poland.

Application for interviews with Mr. Kimens should be addressed without delay to the Comptroller-General, Department of Overseas Trade, 35, Old Queen Street, London, S.W.1. The reference, 4672 T.G., should be quoted in all applications.

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### ROYAL SOCIETY OF ARTS.

On Monday, April 16, the second Cantor Lecture on *Nitrates from Air* was delivered by E. KILBURN SCOTT, M.I.E.E., A.M.-INST.C.E.

On Wednesday, April 18, at the Ordinary Meeting, Mr. HAL WILLIAMS, M.I.MECH.E., M.I.E.E., M.I.STRUCT.E., gave a lecture on *Modern Abattoir Practice and Methods of Slaughtering*. W. Phené Neal, Alderman of the City of London, late Chairman of the Cattle Markets Committee of the Corporation, presided.

On Friday, April 20, at 4.30 p.m., there will be a joint meeting of Dominions and Colonies and Indian Sections. *A Review of the Base Metal Industry, with Special Reference to the Resources of the British Empire*, will be given by SIR RICHARD A. S. REDMAYNE, K.C.B., M.Sc., M.INST.-C.E., M.I.MECH.E., F.G.S.

The Rt. Hon. Lord Emmott, G.C.M.G., G.B.E., will preside.

#### THE GEOLOGICAL SOCIETY OF LONDON.

The following communication was read on March 28, *Further Researches on the Succession and Metamorphism in the Mona Complex*, by EDWARD GREENLY, D.Sc., F.G.S., Dr. Herbert H. Thomas, M.A., Vice-President, in the chair.

At the meeting held on Wednesday, April 18, the following communication was read: *The Structure of the Bowmore-Portaskaig District of Islay*, by JOHN FREDERICK NORMAN GREEN, B.A., F.G.S.

At the meeting to be held on May 2, PROF. J. JOLY, D.Sc., F.R.S., F.G.S., will deliver a lecture on *The Bearing of some Recent Advances in Physical Science upon Geology*.

#### THE INSTITUTION OF ELECTRICAL ENGINEERS.

At the Ordinary Meeting in the Lecture Theatre of the Institution, Savoy Place, Victoria Embankment, W.C.2, on Thursday, April 20, 1923, a paper on *The Drive of Power Station Auxiliaries* was presented by L. BREACH, Member, and H. MIDGLEY, Associate Member.

#### THE FARADAY SOCIETY.

At a general discussion on *Alloys Resistant to Corrosion*, held jointly at Sheffield by the Faraday Society, the Sheffield Section of the Institute of Metals, and the Manchester Metallurgical Society, on April 13, the following papers were read:—

*Heat and Acid Resisting Alloys*, by J. FERDINAND KAYSER, ASSOC. MET.

A short account was given of the "heat and acid resisting" properties of nickel-chromium and nickel-chromium-iron alloys. Most of the literature dealing with this type of alloy has been of a commercial nature, and has contained grossly exaggerated claims concerning the high M.P., resistance to furnace gases, etc. Scientific literature on the subject is somewhat scanty.

The first alloys made in this country were binary alloys consisting of two parts nickel to one part of chromium. Although the addition of chromium to nickel lowers the melting-point until the percentage exceeds 58, alloys containing more than about 50 per cent. of chromium are almost impossible to cast on account of their extreme viscosity. There is nothing to be gained by the use of an alloy containing more than 35 per cent. of chromium. Furnace-parts, case-hardening boxes, etc., if made from a binary alloy, usually contain from 25 to 35 per cent. The alloys with lower percentages are used for resistance wire. Pure

nickel wire was formerly used for that purpose, but was far from satisfactory on account of its tendency to become brittle if used at temperatures above about 700° C. Addition of 10 per cent. of chromium completely prevents this, and nickel-chromium wire can be used at 1,000-1,050° C. without any appearance of brittleness.

The hardness of the alloys increases with increasing chromium, but before the alloys become so hard as to be useful for making a cutting tool, they become very brittle and break under the Brinell ball before showing a hardness higher than about 400.

The high cost of metallic chromium (approximately 5s. per lb.) soon led to the chromium being introduced as ferro-chromium. All alloys containing not less than 10 per cent. chromium together with not more than about 28 to 30 per cent. iron are equally resistant to oxidation, and the permissible percentage of iron depends upon the magnitude of the stress they will be called upon to withstand.

Besides iron, nickel, and chromium there are frequently considerable percentages of other elements present, the most important being carbon, silicon, aluminium, manganese, and copper.

Silicon is often added to nickel-chromium alloys, and up to 2 per cent. the physical properties do not appear to be much affected, but elaborate investigations concerning that point have not been made. The addition of 5 per cent. of silicon and upwards gives an intensely brittle and hard alloy. Such a high silicon also materially reduces the resistance of the alloys to the action of sulphur dioxide.

Nickel and aluminium form an inter-metallic compound NiAl, characterised by a very great heat of formation and a melting-point higher than 1,700° C., i.e., about 300° C. higher than the melting-point of its most difficultly fusible constituent. When aluminium is added to a molten bath of a nickel-chromium, or nickel-chromium iron alloy, there is a violent endothermic reaction and a precipitate is formed. It may seem hard to detect a precipitate in an opaque liquid, but this is not difficult. The examination of microsections of samples quenched out in water from the molten state showed the presence of crystals of such a size and shape that they could not have formed in the solid state, and must have been present in the liquid.

*Corrosion Resisting Properties.*—Nickel-chromium alloys offer a perfect resistance

to the corrosive action of the atmosphere in presence of hard, soft or sea water. Stainless steel should be correctly heat-treated and free from surface scale or pit marks. No heat-treatment is necessary in the case of nickel-chromium alloys. Name plates have been cast with the lettering in relief and exposed to atmospheric action after first sand blasting all over and then grinding the lettering only, and after several years are quite free from corrosion. In towns such name plates become covered with a greenish deposit, but this is identical with that found on window panes, etc., and can be removed as easily.

Samples to be tested were all weighed and measured beforehand. Samples of each alloy were in every case tested at room temperature and 100° C. The duration of the tests was varied for different rates of attack. When necessary, the samples were weighed both before and after the test, and from the loss of weight the rate of loss in grams per sq. metre per hour was calculated.

The alloys were all readily soluble in aqua regia, hydrochloric acid, and sulphuric acid, but not soluble in nitric acid.

Other acids tried were 20, 30 and 50 per cent. acetic, 30 per cent. citric, sulphurous, monochloroacetic, and 75 per cent. phosphoric.

*Monel Metal*, by JOHN ARNOTT, A.I.C.

Monel metal may be said to be primarily an engineering material with excellent physical properties and good resistance to many corrosive agencies. Its sphere of use is therefore different from that of the truly acid-resisting metals, such as the iron-silicon alloys, which have to be employed in certain cases in spite of their poor mechanical properties.

Its composition and physical properties are fairly well known. Cold-rolled and cold-drawn metal are now used to quite a considerable extent.

An important property is its retention of strength and ductility at temperatures above normal.

At 750° F., the highest steam temperature in use in this country, monel metal retains 85 per cent. of its strength.

Monel metal is very little affected by exposure to fairly pure air. A sheet freely exposed to the elements at Cathcart was bright after five months and showed no change in weight. In air which is most impure, it becomes discoloured, but the attack does not extend beyond the surface layers.

It is unaffected by wet, saturated or superheated steam. Sea water does not affect it.

Monel metal usually is not suitable for use with strong acids, as in acid manufacture. It is readily soluble in concentrated nitric acid, and is attacked by strong hydrochloric and sulphuric acids, especially if they are impure. Sulphurous acid, even when very dilute, attacked monel metal violently, leaving a deposit, largely consisting of sulphide.

Monel metal is not affected by alkalis and only to a slight extent by the majority of solutions of neutral salts at ordinary temperatures.

Monel metal is thus suitable for parts which have to resist (1) sea water, (2) impure water such as is found in many canals and in mines, (3) steam, (4) dilute acid solutions such as are used in many industrial operations, (5) alkaline solutions of all kinds.

*The Mechanism of the so-called "Dry Corrosion" of Metals*, by ULICK R. EVANS.

Experiments on the behaviour of "apparently dry" metals, roughened with emery, show that no corrosion occurs when they are kept over sulphuric acid, and only slow, superficial corrosion when they are kept over water. The rate of attack is greatly increased by the presence of volatile electrolytes in the air, sulphur dioxide being most dangerous to iron and nickel, ammonia to copper and its alloys, and hydrogen chloride to zinc and aluminium; hydrogen sulphide and carbon dioxide somewhat increase the rate of rusting of iron, but produce only superficial changes on other metals. Contrary to popular belief, the corrosion of iron is not caused by the presence of ammonia. Corrosion of metals by volatile electrolytes appears to require the presence of some moisture, but proceeds in air which is distinctly unsaturated. Special phenomena occur at the contact of dissimilar metals, apparent electrochemical protection being observed in some cases.

The phenomena are best explained if we consider that electrochemical action occurs in the adherent (usually invisible) film of moisture. Volatile electrolytes increase the conductivity of the film and thus accelerate corrosion. Where they tend to produce hygroscopic corrosion-products, they bring about the absorption of further moisture and thus increase the thickness of the film; in several cases (zinc in hydrogen chloride, copper in ammonia, nickel in sulphur di-

oxide) the metal, originally dry, soon begins to shed liquid copiously, and in such cases corrosion is very serious.

*The Resistance to Corrosion of Stainless Steel and Iron*, by J. H. G. MONYPENNY, Chief of the Research Laboratory, Brown Bayley's Steel Works, Ltd., Sheffield.

To the almost exclusive use of stainless material for cutlery purposes over a considerable period may be ascribed the opinion that stainless steel has a definite composition and a small range of mechanical properties. There is, however, a whole range of steels in which the main variable is carbon, precisely in the same manner as this element is the prime factor in producing hard and soft steels. In addition to this the presence in varying amounts (either through accident or design) of other elements such as silicon, manganese, or nickel may have appreciable effects. Variations in one or more of these elements may have quite appreciable effects on the resistance to corrosion of the stainless material.

In addition to differences in chemical composition, the properties of the material may be profoundly modified by varying forms of heat treatment, and such variations have pronounced effects on the degree of resistance to corrosion.

Heat treatment—hardening, tempering and annealing—all influence the final products in various ways.

A study has been made of the resistance of stainless material to various corroding agents.

Tap water is without action on stainless steel, either hardened, or hardened and tempered. The author has had a number of small samples turned from a hardened and tempered bar over which tap water had been allowed to trickle for over twelve months, and there is not the slightest signs of attack. These samples are contained in a wide glass tube attached to a water tap, the latter being opened slightly, thus allowing water to trickle over the samples.

Samples of stainless steel and iron in the hardened and tempered condition were partly embedded in a block of wood and the latter then fixed to a jetty at a point between high and low water marks. The samples were thus alternately wet and dry. After six months they were quite bright and practically unattacked, there being only a few minute pits.

River and well waters have in general no appreciable action on stainless material. This is shown by the large number of pump



rods and other fittings which are in successful use in many parts of the country for pumping such water.

Ammonia, alkalies and alkaline carbonates in all strengths of solution appear to have no effect on stainless material.

It may be doubted whether the results of experiments in which samples of stainless steel (or any other metal) are placed or suspended in beakers containing solutions of various salts are of any great practical value. The results obtained simply refer to the conditions under which the test was carried out, and will vary as these conditions vary. With stainless material, when corrosion does take place, it almost invariably starts at the point of support, and often is entirely confined to that point. In such cases, therefore, the amount of corrosion, or even the presence or absence of corrosion, will depend on how the sample is supported. It is not intended, therefore, to give a list of how stainless samples behaved when immersed in various solutions. Speaking generally, it may be said that many such solutions have little or no effect on stainless material, and where corrosion does take place it proceeds much slower than with ordinary steel.

The results with solutions of a few salts, however, are of some interest.

Ammonium chloride solutions are well known as corroding agents. They have a staining and pitting action on stainless material the extent of which, however, depends on the concentration of the solution. With dilute solutions the attack is very slow, even when hot.

Ferric chloride solutions attack the steel even when fairly dilute (*e.g.*, 1 per cent.).

Copper chloride solutions also attack the steel. With strong solutions a deposit of copper is formed, and the steel is eaten away fairly rapidly. With dilute solutions, on the other hand, pitting takes place and very little copper is deposited.

Copper sulphate, nitrate, and acetate solutions, on the other hand, have no action on the steel. The presence of copper sulphate also appears to retard greatly, and in some cases to prevent the attack of dilute sulphuric acid on stainless material.

Hydrochloric and sulphuric acids attack stainless steel or iron rapidly. The action of these acids on high chromium steels has been known for a considerable time, and hence it is not necessary to devote further attention to them. Sulphurous acid also attacks stainless material, probably to some

extent owing to the presence in it of sulphuric acid.

*Nitric Acid.* — The attack of nitric acid present several interesting features. Very dilute solutions attack stainless material slowly, the rate of attack decreasing with increasing content of chromium, and with decreasing carbon content. The stronger acids used in analytical work (*e.g.*, S.G. 1.20 and 1.42) are practically without action on the steel. This fact appears to be fairly known, and since acids of S.G. 1.20 attacks ordinary steel very rapidly this reagent is useful should stainless material be accidentally mixed up with ordinary steel. With prolonged attack (*e.g.*, lasting a month or six weeks) of acids of these strengths, the surface of the steel is coloured a purplish tint but there is no appreciable alteration in weight. The colour thus produced bears some resemblance to a "temper colour," and is probably of a similar type to the latter. If a polished microsection be treated in this way, it is found that the background is coloured while the carbide remains brilliantly white.

With a typical stainless steel containing 0.32 per cent. carbon and 12.2 per cent. chromium the maximum attack with dilute acids (at atmospheric temperatures) occurred at about normal strength.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

The Friday evening discourse on April 20, at 9 o'clock, will be delivered by W. J. S. LOCKYER, M.A., F.R.A.S., Director, Norman Lockyer Observatory. The subject is *The Growth of the Telescope*.

On Tuesday, April 17, SIR ARTHUR KEITH, M.D., LL.D., F.R.S., Sec. R.I., Fullerian Prof. of Physiology, gave a lecture on *The Machinery of Human Evolution: How Old Structures are Lost*.

On Thursday, April 19, PROF. A. O. RANKINE, O.B.E., D.Sc., lectured on *Transmission of Speech by Light*. (Lecture II.).

At a General Meeting of the members of the Royal Institution, held on the 9th inst., the Duke of Northumberland (President), in the chair, a resolution of condolence with Lady Dewar on the death of Sir James Dewar was moved by the President and carried unanimously.

Mr. Arrol Moir, Professor A. O. Rankine, Lady Wallace, and Miss Williamson were elected members.

#### SOCIETY OF GLASS TECHNOLOGY.

The Sixth Annual General Meeting of the Society was held in Sheffield, on Wednesday, April 18, 1923.

After other business, the Presidential address, entitled, *The Year in Review in the World of Glassmaking*, was delivered.

Afterwards a general discussion on *Works Organisation*, opened by a paper entitled *Organising for Production from Pot Furnaces*, by W. W. WARREN, A.M.I.C.E., A.M.I.E.E. Other speakers presented the case for Tank Furnace Works.

#### FIFTH ANNUAL DINNER.

The attention of members is directed to the fact that the Fifth Annual Dinner of the Society will be held this year in London, following the meeting on May 16.

Members are requested to keep this date open so that a good attendance may be assured. Full particulars will be announced later.

#### THE CHEMICAL SOCIETY.

At the Ordinary Scientific Meeting, on Thursday, April 19, the following papers were read:—

*The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. Part VII. Reactions of 2:5- and 4:5-dinitro-m-xylenes*, by K. IBBOTSON and J. KENNER.

*The Chemistry of the Three-carbon System. Part I. The Influence of the cyclohexane ring on the  $\alpha\beta$ -By Change*, by S. F. BIRCH, G. A. R. KON, and W. S. G. P. NORRIS.

*On the promotion of Catalytic Reactions. Part I.*, by S. MEDSFORTH.

#### PHYSICS AND SEWAGE DISPOSAL.

At a meeting of the Birmingham and Midland Section of the Society of Chemical Industry, on Tuesday, April 10, this subject was discussed in an important paper by Mr. F. R. O'SHAUGHNESSY, A.R.C.Sc., F.I.C., Consulting Chemist to the Birmingham, Tame and Rea District Drainage Board.

The paper was a thesis dealing with the physical properties of the principal compo-

nents of normal sewage (*i.e.*, of the water on the one hand and the usual polluting bodies on the other) as affecting those operations preliminary to disposal, comprised under the heading of "Treatment," which are of a preparatory character and for the purpose of facilitating disposal.

To this end the published work of a number of leading experts is critically reviewed in support of the views advanced by the author.

A clear distinction is made between "Treatment" and "Disposal."

Emphasis is laid on a statement of Fowler's, *viz.*: "The subject of sewage disposal is mainly a question of the separation of solids from liquids."

This separation has been difficult because of the physical character of much of the solid matter present in sewage, *viz.*: its colloidal or gummy character, which causes it to adhere tenaciously to water.

The author refers to his own published results, showing:—

That faecal solids pass into colloidal solution in water by agitation to 200-250 parts per 100,000;

That this is the chief source of colloidal solids in normal sewage;

That the amount varies in different sewages.

The effect of various methods of treatment of sewage are discussed: Simple sedimentation, chemical precipitation, biological action (anaerobic and aerobic). It is shown that whereas the visible suspended solids in sewage are for the most part readily separated, the bulk of the colloidal solids are held very tenaciously by the water of the sewage.

The colloidal solids are very partially thrown down by simple sedimentation. Chemical precipitation effects only partial removal even when large amount of chemicals are added, and when in moderate amount improves the liquor for the bacteria bed. Anaerobic action, whilst removing colloids, makes the liquor very offensive; aerobic treatment is the only means of precipitating colloidal solids whilst leaving the liquid in a satisfactory condition.

It is known that as aeration is effective and complete so the rate of removal of these troublesome solids is also effective.

That considerations of this character and the observed suddenness with which they are brought down in the top of a percolation bed suggest that, given an appropriate

agent, their removal should be easy and rapid.

The remarkable work of F. Wallis Stoddart, F.I.C., F.C.S., is reviewed, which indicated that given a limpid sewage liquid which had been freed from colloidal solids by appropriate means, the quantity of liquid which could be put through a suitable percolation bacteria bed might be immensely increased, even to 10 or 20 million gallons per acre. The author then indicates that the technique provided by Messrs. Ardern and Lockett in the activated sludge process has furnished the key to the solution of this problem. That a modified use of this technique which for purposes of distinction the author proposed to call the flocculated sludge process, is the appropriate means of dealing with colloidal matter in solution.

In regard to the activated sludge proposition, the merits and demerits are discussed. Advantages are: Completion of sewage purification in one tank in one operation; elimination of nuisance, reduction of area, and production of valuable fertilizer.

The objects are: Existing works discarded; sludge problem more complex; economical recovery of sludge problematical; extravagant, *i.e.*, prolonged aeration, high oxygen demand by sludge, alteration of physical character of sludge, etc.; slow rate of solution of oxygen in water the central physical fact here; in many cases protection required for aeration. The procedure in this process is arbitrary, its objective largely commercial (conserving manurial elements) and must stand or fall on financial merits.

As to flocculated sludge process (a modification of the activated sludge process), three operations are involved: Agitation of sewage and flocculated sludge with air for a time to bring about clarification of the sewage and partial purification of the liquor; separation of sludge from treated sewage, and re-aeration of separated sludge.

This mode of procedure may be applied to the whole sewage (less grit, etc.) as in the activated sludge process or after any desired degree of preliminary sedimentation. The advantages are: A wide choice of procedure is available, for the process may be incorporated with existing plant; greatly increased volumes of liquid may be put on bacteria beds; nuisance (odour and flies) may be eliminated; and the expensive aeration period may be reduced to reasonable proportions.

The theory of flocculated sludge process is next discussed. Evidence is given that

the purification of sewage is effected by two distinct means: By physical agents which bring about flocculation of colloidal solids; and by biological agents which bring about oxidation of the dissolved impurities. In the activated sludge technique the real flocculating agent is the sludge. Evidence is given that the condition of the sludge is much more important than its quantity, and that with the procedure advocated in the flocculated sludge process very remarkable and rapid purification may be obtained with greatly reduced volume of sludge. Thus the flocculated sludge is apparently the vehicle for the transference of energy. By eliminating easily separable material from the sewage the oxygen demand of unprofitable or useless elements is reduced and consequently the efficiency of the action very greatly increased.

The whole question of sludge treatment is presented thus:—

The bulk of the solids may be separated from the bulk of liquid in the crude sewage quite readily.

When separated, the peculiar physical properties of the solids assert themselves thus: (a) The solids (sludge) adhere most tenaciously to about 9 times their weight of water; (b) the sewage liquor adheres with great tenacity to about 20-25 per cent. of the solids of the original sewage.

The problem presented in each case is the same, *viz.*: the modification of the physical character of the colloidal solids.

In the case of the sludge this change is conveniently effected by the inoffensive intensive, anaerobic digestion of the sludge as by the Imhoff Tank or by the method of separate digestion as at Birmingham (England), and Baltimore (U.S.A.), and elsewhere. It is claimed that the cost of the latter method is relatively low.

#### NOTE ON THE PREPARATION OF SARCOLACTIC ACID.

By JOHN MISSENDEN, B.Sc.

This substance, also known as  $\delta$ - $\alpha$ -hydroxypropionic acid,  $\delta$ - $\alpha$ -CH<sub>3</sub>.CH(OH).CO.OH, may be prepared from proteinous tissue, mainly intercostal, by boiling the flesh for several hours until the fibres separate and present a greyish appearance. The liquid so obtained, subsequent to filtration, is fairly abundant in sarcolactic acid, and should be carefully evaporated to a thick syrup, care being taken that no burning on

the sides of the vessel takes place. Immersion of this vessel in strong brine is a satisfactory process.

While at a temperature of about 40° C., 2.5 volumes of alcohol (75 per cent.) should be added, and the whole made up to 6 volumes with water. Again, the evaporation to a syrup takes place, and the whole is slightly acidified with a few drops of sulphuric acid, and filtered. The acid is then extracted with ether, and purified by conversion into a convenient metallic salt.

This method of preparation takes several days, but seems the speediest way of obtaining the pure product. There is no objection to assisting the filtration of the acidified extract by the careful addition of water, but subsequent procedure makes this undesirable. Muscular tissues surrounding the abdomen and femur in the human body form a plentiful source of the substance, but the regions of the lactic organs at the front of the thoracic cavity yield the best supply.

#### GENERAL NOTES.

#### DYESTUFFS (IMPORT REGULATION) ACT.

##### APPLICATIONS FOR LICENCES IN MARCH.

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during the month of March, 1923, has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee.

The total number of applications received during the month was 539, of which 459 were from merchants and dealers. To these should be added the 30 applications outstanding on 1st March, making a total for the month of 569. These were dealt with as follows:—

*Granted.*—405 (of which 376 were dealt with within seven days of receipt).

*Referred to British makers of similar products.*—105 (of which 96 were dealt with within seven days of receipt).

*Referred to Reparation supplies available.*—37 (all of which were dealt with within two days of receipt).

*Outstanding on 31st March.*—22 (mostly received immediately prior to Easter).

Of the total number, 569, of applications

received, 467, or 82 per cent., were dealt with within four days of receipt.

#### IMPORT OF CHEMICALS INTO GUATEMALA.

The Acting British Vice-Consul at Guatemala reports that by virtue of an Ordinance, dated 30th December, 1922, and published in the "Official Gazette" of 23rd January last, certain chemical and medicinal substances may be imported by persons not licensed as pharmacists or druggists.

A list of such chemical and medicinal substances is available and may be consulted by United Kingdom firms interested on application to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1. (Reference 7683/F.L.).

#### ECLIPSE TESTS.

##### FURTHER CONFIRMATION OF EINSTEIN'S THEORY OF RELATIVITY.

The photographs of the total eclipse of the sun last September have now been carefully examined and measured. Compared with their real positions, the stars thus photographed near the eclipsed sun all showed the displacement which should appear, supposing Einstein's theory to be true.

Close on the announcement that the Canadian plates show practically the Einstein shifts comes news from the Lick Observatory of similar confirmation. The Lick expedition, which went to Australia, was very elaborately equipped for the purposes of the test, and obtained a series of photographs of the region around the eclipsed sun which showed over eighty stars, some of them as faint as the tenth magnitude. The mechanical work of measuring the plates for star positions, which necessitated determining them with accuracy to a small fraction of a second (or on the scale of the plates to about the 5,000th part of an inch), and the mathematical discussion of the actual values of the displacements has taken several months.

Thus Relativity has successfully survived the two eclipse tests to which it has been subjected, that of 1919 and that of last year.

## NOTICES OF BOOKS.

*Atomic Theories*, by F. H. LORING. Second edition, revised. Pp. XII. + 218. London: Methuen & Co., Ltd., 36, Essex Street, W.C.2. 1923. 12s. 6d. net.

During the last few years, atomic and sub-atomic science has developed so greatly that only the specialist has been able to keep well-informed by careful and constant perusal of the original literature. Mr. Loring's volume on the atomic theories has therefore been of great service for the general scientific reader anxious to gain a clear, comprehensive, and up-to-date knowledge of this subject.

The author has availed himself of the opportunity afforded by the publication of a second edition to introduce the results and conclusions of investigations which have been announced since the first edition (reviewed in *The Chemical News*, 1922, CXXIV., 158) appeared.

It may be pointed out that the tetrahedral arrangement of the carbon atom given in Fig. 19, page 90, is not adhered to on page 110, Fig. 33. Presumably the author had in mind that the electrons might shift their positions in the carbon atom to meet the positions in the attached oxygen atoms. The tetrahedral arrangement in the carbon atom would obviously do equally well, for one oxygen atom need only be orientated accordingly.

The additions include the author's *Wedge Periodic Table of the Elements*, and a fuller table of isotopes is given on pages 191 and 193.

A few minor corrections have also been made, and difficult passages re-written, so that the book can now claim to be a standard work, since it deals with all the theories relating to the atom, and discusses their experimental foundations. It will be read by an increasing number of students of Chemistry and Physics, and by others interested in the latest developments and views concerning the Atom.

*Surface Tension and Surface Energy, and their Influence on Chemical Phenomena*, by R. S. WILLOWS, M.A., D.Sc., and E. HATSCHEK. Third Edi-

tion. Pp. VIII. + 134, with 25 illustrations. London: Messrs. J. & A. Churchill, 7, Great Marlborough St. 1923. 6s. 6d. net.

The exposition of main physical properties of the subject, together with absence of a quantity of tedious calculation seems to be the keynote of this edition; in which has been added some important notes upon the properties of thin films, polarised molecules, and boundary lubrication. As Dr. Willows explains in his preface, the work indicates the possible connections between surface tension and other chemical and physical properties of liquids, "and . . . opens up many fascinating avenues for research."

Some confirmed observations of Eötvös, the Hungarian chemist, have been dealt with, in order to show how these relationships are more or less apparent, and the evolution of Dr. A. Ferguson's formula (*Phil. Mag.*, Jan., 1916),  $\sigma\theta = \sigma_0(1-b\theta)^n$  for showing the dependence of surface tension upon critical temperature is of interest. On p. 123 is a brief paragraph incorporating some points upon the various stages of tanning, and their facilitation by means of the electric charge (i.e., the electro-combination of the tannins).

The work is an old favourite, and the present edition should prove of even greater value to biologists and chemists. We can well recommend it to those engaged in the study of colloidal principles.

*The Spectroscope and its Uses in General Analytical Chemistry*, by T. THORNE BAKER, A.M.I.E.E., F.R.P.S. Second Edition. Pp. X. + 208. London: Messrs. Baillière, Tindall & Cox, 8, Henrietta Street, Covent Garden, W.C.2. 1923. 7s. 6d.

The vast development of spectroscopy has been responsible for considerable extensions in this work. In 1907, when the first edition was issued, the spectroscope was not sufficiently developed to render it so highly important in quantitative analytical processes, although its efficiency was fully recognised. Now, the most modern instruments and their most recent applications have necessitated much of the text being recast.

Laboratory usages have been dealt with in an extensive manner, spectrophoto-

graphy taking prominent space. The book would hardly be complete without giving details of the infra-red spectrometer of Messrs. A. Hilger, Ltd., which the author has described and illustrated in a manner clearly demonstrating the fundamentals of series-reflection-refraction through the thermopile-slit.

In the final chapter, attention is paid to the X-ray spectra. The examination of metals by this means has produced some new results which are discussed throughout the brief treatise upon the subject; but greater attention could have been paid to the monochromatic-radiation filters, which must vary with the substance examined, and the nature of the anti-cathode target.

Good illustration (for which Messrs. A. Hilger, Ltd., Watson Sons, Ltd., and J. J. Griffin & Sons, Ltd., are largely responsible) and compositorial excellence crown a very lucid and self-explanatory text; a most useful work in every way.

We are in receipt of *Skinner's Cotton Trade Directory for 1923*. (London: Messrs. Thomas Skinner & Co., Gresham House, London, E.C.2. Price 12s. 6d. net). It is a handy and compact volume, and contains much information of value to those interested in the personnel and progress of the cotton industry.

The proprietors of *Current Opinion* (The Industrial League and Council, 82, Victoria St., London, S.W.1) have sent us their "first birthday" number. The general tone of the publication tends to be optimistic of trade revival, and figures are quoted which justify the optimism. There is little doubt that such periodicals as *Current Opinion* help greatly in the co-ordination of individual enterprise, and we wish the proprietors and editor, G. C. Lawrence, Esq., every success.

The issue of *Nature* for April 7 contains further correspondence relating to the discovery and identity of Hafnium.

In a letter *On Urbain's Celtium Lines*, H. M. Hansen and S. Werner, of *Universitetets Institut for teoretisk Fysik, Copenhagen*, write:

Through an examination of the very careful measurements of the spectra of the rare earths published during the last few years by Eder, we have learned in the meantime that the greater part of Urbain's celtium lines have been observed by this author (*Wiener Ber.*, IIa, vol. 124, 1915) in the spectrum of a preparation of the rare earth

element cassiopeium or lutetium. The discovery of this element (atomic number 71) was announced in 1905 by Auer von Welsbach, to whom the former name is due, while the name lutetium was proposed in 1907 by Urbain, who published at the same time the first list of lines of its optical spectrum (*Comptes rendus*, t. 1907, 145, p. 759).

In the table they give the wave-lengths of the celtium lines from Urbain's paper and the corresponding wave-lengths and intensities from Eder's measurements of the cassiopeium spectrum.

There is close accordance in the values of the relative intensities in the two cases, which we think justifies the identification of the lines also in the few cases where the difference between the wave-lengths is slightly greater than is to be expected from the usual accuracy of Urbain's measurements of wave-lengths or rare earths. Only a few of these lines, denoted by an asterisk, were included in Urbain's original list of the lutetium lines.

It is of interest to add that in a recent note (*Comptes rendus*, t. 176, 1923, p. 496), which first came to our notice after the above was written, dealing with the discovery by Coster and Hevesy of the element hafnium with atomic number 72, Urbain himself directs attention to the particular behaviour of the lines ascribed by him to celtium, and expresses the conjecture that these lines—the observation of which was the basis for his belief in the presence of a new element in his preparation—may actually constitute the spark spectrum of the element 71.

D. Coster and G. Hevesy also contribute another letter *On Celtium and Hafnium*. Among other matters they state:

Only two lines of the element 72 were claimed to have been detected by Dauvillier, and even in the case of the most intense of these lines we meet with the difficulty that it falls in the same place in the spectrum as the strongest zirconium line in the second order. As an argument against ascribing this line to zirconium, Urbain states that the optical spectrum of his preparations did not show any zirconium line. An investigation of Urbain's spectrum of the "celtium" preparation, however, does not show any line of the hafnium spectrum either. If the possibility of the presence of one of these elements in Urbain's preparation can be taken seriously into consideration, it should be expected that zirconium would be present in greater amount. In

fact, zirconium was likely to be more abundant in the original mineral than hafnium, and a purification of rare earth preparations from zirconium and not simultaneously from hafnium, by treating with oxalic acid or any other method mentioned by Urbain, is scarcely imaginable in view of the close similarity of the chemical properties of these elements. As mentioned in our previous letters, however, the two lines ascribed by Dauvillier to the element 72 were lying 4 X-units distant from our Hf-lines, which is distinctly more than the limit of experimental error,<sup>1</sup> whereas the lines of the elements 70 and 71 measured by Dauvillier (*Comptes rendus*, vol. 174, p. 1347, 1922) on the same plates closely agree with the measurements of the same elements obtained by Coster (*Phil. Mag.*, vol. 44, p. 546, 1922). As the two lines according to Dauvillier were extremely faint, they may easily be explained to be of some other origin.

It is of interest to note that, at various times, announcements have been made as to the complexity of zirconium. In 1845 Svanberg claimed that in decomposing zircons he discovered a new element, "norium," with a lower atomic weight than zirconium. His and Sjögren's (1853) statements were later disproved by the work of several investigators, including Marignac. In 1864 Nylander reported the existence of two earths in zircona. Five years later, by a spectroscopic investigation of zirconium, Sorby was led to announce the discovery of "jargonium" and Church of "nigrium." Finally, in 1901, Hofmann and Prandtl thought that they had found in euxenite a new element related to zirconium. It is also interesting to note that Mendeleëff, as we learn from Sir T. E. Thorpe's letter in *Nature* of February 24, p. 252 (March 17), suggested that the extraordinarily discordant values for the atomic weight of titanium, found by several chemists, might be due to the presence of a homologous element of higher atomic weight in their material. Whether these statements in some cases may be explained by the presence of hafnium in the minerals and preparations under investigation, it is

<sup>1</sup> *Dauvillier's measurements carried out since the announcement of our discovery, on other material which possibly contained hafnium, have already led him to give new values for the same wave-lengths, which are respectively 3.4 and 2.3 X-units larger NATURE, February 17, 1923).*

not easy to decide. The intricate chemistry of zirconium, and the great chemical similarity of hafnium with this element, would in fact have made any establishment of hafnium very difficult before the development of the powerful method of X-ray analysis.

*A Tested Method of Laboratory Organisation*, by SEYMOUR PILE, M.A. (CANTAB), and REGINALD G. JOHNSTON, with an introduction by W. R. BARCLAY, O.B.E. Pp. XI. + 98. London: H. F. & G. Witherby, 326, High Holborn, W.C. 1923. 7s. 6d. net.

Birmingham brass-founders followed a commendable course when they entered upon their co-operative laboratory scheme, and put into being the Midland Laboratory Guild, Ltd. The hundreds of little brass-works in and around the district were sadly lacking in efficient laboratory services until this great centre was established; now they have facilities at least equal to those possessed by the enormous steel firms of Lancashire and Yorkshire.

Such a laboratory needs first-class organisation, and Messrs. Pile and Johnston have described in their book how this has been attained. Not only the construction and equipment of the building have been dealt with, but also the personnel and the methods of analysis and costing; and the masterly manner of enumeration tells of considerable familiarity with the inner detail of the processes.

The chapter upon *The Scientist in Relation to This, That, and the Other* is something unusual. It takes the scientific mind to pieces, exposing all the works. Some of these works, reduced to their first principles, are a trifle astounding, as they typify the scientist on the lines of human perfection, and give one the impression that the analytical chemist is the nearest approach to the ideal. This has the effect, as do most other chapters in the book, of creating an inspiring atmosphere around the study of chemistry, and promoting what is essential to the scientist—a love for his work.

Altogether, the book must prove valuable. The methods it describes are efficient, and will have some significant bearing upon future laboratory management; while, as a text-book, it provides excellent scope for the foundation of new ideas. Messrs. Pile and Johnston are to be congratulated upon it, and wished every success.

We have received a copy of the 1923 issue of the *Directory of Paper Makers of the United Kingdom*, price 5s. 9d. net. It has again been authentically revised and brought up to date, and contains information valuable to all connected with this industry.

It includes alphabetical lists of paper makers; paper enamellers, surfacers and gummings; mills; trade designations; paper trade customs, and other useful matter.

The following Bulletins have been published by the Department of the Interior, United States Geological Survey:—

*Gold and Silver in 1921*, by J. P. DUNLOP.

*Stone in 1921*, by G. F. LOUGHLIN and A. T. COONS.

*Cement in 1921*, by BELLE W. BAGLEY.

*Natural Gas Gasoline in 1921*, by E. G. SIEVRES.

*Potash in the Greensands of New Jersey*, by GEORGE RODGERS MANSFIELD (1922).

*Surface Water Supply of the United States, 1918. Part IX.: Colorado River Basin.*

*Copper Deposits of the Tyrone District, New Mexico*, by SIDNEY PAIGE, 1922.

#### BOOKS RECEIVED.

*Ink*, by C. AINSWORTH MITCHELL, M.A., F.I.C. Pp. VIII. + 128. 1923. Sir Isaac Pitman and Sons, Ltd., Parker Street, Kingsway, W.C.2. 3s. net.

*Einführung in die Kolloidchemie*, von PROF. VIKTOR POSCHL. Pp. XII. + 158. 1923. Verlag von Theodor Steinkopff, Dresden und Leipzig. 3s. 11d. net.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

7828—Deschamps, J. J.—Facilitating physical or chemical reactions in piled bodies. March 19.

8120—Farbenfabriken vorm., F. Bayer & Co.—Manufacture of azo-dyes. March 21.

7813—Verein für Chemische und Metallurgische Produktion.—Production of chemically-pure hydrochloric acid. March 19.

194339—Rardt, H.—Process for precipitating or recovering metals from their solutions.

194625—Douglas, R. P.—Manufacture of sulphate of ammonia.

185124—Mathesius, W., & H.—Process for producing lead alloys containing strontium.

192438—Dyes; intermediate products.—Akt-Ges für Anilin-Fabrikation, Berlin.

*o-Oxyazo dyes* are prepared by coupling a diazotized dihalogen-2-aminophenol, containing as a fifth substituent a halogen atom or an alkyl group, with an oxynaphthalene sulphonic acid or a substitution product thereof other than 8-halogen-1-oxynaphthalene-5-sulphonic acid. Examples are given of the preparation of dyes from the following pairs of components:—3: 4: 6-trichlor-2-aminophenol and 1-naphthol-5-sulphonic acid; 3: 4: 5-trichlor-2-aminophenol and 1-acetylamino-8-naphthol-4-sulphonic acid; 3: 4: 5: 6-tetrachlor-2-aminophenol and 2-naphthol-6-sulphonic acid; 4-methyl-3: 5-dichlor-2-aminophenol and 1-acetylamino-8-naphthol-4-sulphonic acid; these dye wool with chrome mordants reddish-blue, blue, reddish-violet, and reddish-blue shades respectively. The following second components also are specified:—1-naphthol-4-sulphonic acid, 1-amino-8-naphthol-4-sulphonic acid, 1-amino-8-naphthol-2: 4-disulphonic acid, 1-benzoylamino-8-naphthol-4-sulphonic acid, 1-*p*-toluenesulphamino-8-naphthol-4-sulphonic acid, 1-phenylamino-8-naphthol-3: 6-disulphonic acid, 2-benzoylamino-5-naphthol-7-sulphonic acid. Specification 168,681 is referred to.

3: 4: 6-Trichlor-2-aminophenol is made from 1: 2: 4: 5-tetrachlorbenzene by replacing one chlorine atom by an hydroxyl group, nitrating, and reducing.

3: 4: 5-Trichlor-2-aminophenol is made from 3: 4: 5-trichloraniline by diazotizing, boiling, nitrating, and reducing.

4-Methyl-3: 5-dichlor-2-aminophenol is made from 4-amino-2: 6-dichlor-1-methylbenzene by diazotizing, boiling, nitrating, and reducing; the 4-amino-2: 6-dichlor-1-methylbenzene is prepared by dichlorinating 4-nitrotoluene and reducing.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the price of 1s. 6d. each.

#### PAMPHLETS.

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# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3289.

## CHEMICAL INDUSTRY AND THE BRITISH EMPIRE EXHIBITION (1924).

For the first time in the history of great exhibitions, the chemical industry is to be represented in all its branches. Hitherto, manufacturers have not taken sufficient interest in such displays; in the main, for two reasons. Firstly, the reputation of British heavy chemicals was, presumably, too well established to warrant representation; and, secondly, fine chemicals and dyestuffs were too undeveloped to admit of the manufacturers thereof indulging in such heavy expenditure.

Quoting from the *Empire Exhibition News* (February, 1923), about 50 firms have been entered. Home alkalis and the complete range of coal by-products will be exhibited, as well as fine chemicals and domestic materials. A most interesting feature will be the presence of the leading scientific societies for the purpose of illustrating the progress of pure and applied chemistry during the past 10 years; this will cover the period of the late war.

As the European upheaval depressed the industry, so will the Exhibition more than revive it. Dyestuffs, certainly, will benefit; while the general lines of future research will be more in co-ordination with industrial requirements.

Organisation of the Chemical Section is being undertaken by the Association of British Chemical Manufacturers, and it is to be hoped that firms will do their utmost to arrange for exhibits—to the benefit of all concerned.

J. M.

## THE PROBLEM OF SUBSTITUTION IN THE BENZENE NUCLEUS AND THE THOMSON-LEWIS-LANGMUIR THEORY OF CO-VALENCE.

By RONALD FRASER AND JAMES ERNEST HUMPHRIES.

(Continued from Page 245.)

The electromer present in greater concentration—a factor evidently determined by the relative octet stabilities of  $X_1$  and

$X_2$ —will react with greater velocity with the entering group; and the resulting tri-substituted compound will predominate in the final products. If  $X_1$  has the greater octet stability, further substitution will take place at the 4 and 6 positions; if  $X_2$ , at the 3 and 5 positions; i.e., considered from the standpoint of  $X_1$  alone, ortho-para if  $X_1$  is negative and meta if  $X_1$  is positive. If the octet stabilities of  $X_1$  and  $X_2$  are widely different, one electromer may be present in such small concentration that its resultant will not be capable of detection in the final products. On the other hand, if the octet stabilities of  $X_1$  and  $X_2$  are of the same order, the number of products will be greater. The two possibilities may be illustrated by the iodination of o-toluidine (Wheeler and Liddle, *Amer. Chem. J.*, 1909, XLII., 501), and the nitration of o-chlorotoluene (Wibaut, *Rec. Trav. Chim.*, 1913, XXXII., 244).

Similar reasoning applies to disubstituted derivatives of the type  $C_6H_4 X_{1(1)} X_{1(4)}$

Case 2, Fig. 3, ii. In this case the octet tendencies of  $X_1$  and  $X_2$  reinforce each other, and a single electromer exists. Substitution would be expected to occur at the 4 and 6 positions, which is in agreement with the facts.

Case 3. This is similar to Case 1. If the octet instability of  $Y_1$  is greater than that of  $Y_2$ , electromer (a) will predominate, and if conversely, electromer (b). Further substitution will proceed accordingly.

The type  $C_6H_4 Y_{1(1)} Y_{2(4)}$  is similar.

Case 4. A single electromer. Further substitution at 5.

Case 5. A single electromer. The groups X and Y reinforce each other's natural octet tendency. The smooth nitration of the nitrophenols is all in agreement with this statement. The type  $C_6H_3 X_{(1)} Y_{(4)}$  falls under this case.

Case 6. Equilibrium between electromers holds in this case; reference to Postulate 2 indicates that the direction of equilibrium will be that shown (Fig. 3, vi.), and hence ortho-para directive substituents will exert the greater influence in orientation.

### THE EFFECT OF CONDITIONS.

One of the main difficulties to the formulation of definite rules summarising the facts of orientation is the effect of conditions in altering the relative amounts of the final products of a reaction. On the octet view, this means that the equilibrium

pictured above in the electromeric equations, or, in the cases where a single electromer exists, the relative octet stabilities of the substituents, is altered. In either instance, this would indicate that the effect of conditions is largely one of electron transference.

The work of Biltz (*Z. Elek.*, 1911, XVII., 676) has shown that carbon possesses a very high characteristic vibration frequency; and, as stated by W. C. McC. Lewis (*System of Physical Chemistry*, vol. III., 62), "an atom possessing high frequency is no doubt the most likely type of atom to allow of the transference of electrons to and from itself." That electron energy increases with rise of temperature has been indicated by Koenigsberger (*Z. Elek.*, 1911, XVII., 289), and electron lability must also be affected by the nature of the solvent medium (dielectric constant, etc.). It is along these lines that we hope to approach the problem of conditions.

#### REPLACEMENTS AND OCTET STABILITY.

The term "Replacement" is used to denote the exchange of one substituent for

another; "Substitution" refers to the exchange of hydrogen for an entering group. It seems to us that no essential distinction can be drawn between the two processes; and we regard substitution merely as a special case of replacement. No rule of replacement corresponding to a rule of substitution has, so far as we can find, been formulated; but consideration of our remarks on the special case of the "octet stability" of hydrogen appears to lead to some degree of uniformity in this respect. It was pointed out that the lability of hydrogen was conditioned by its tendency to give up its electrons; whereas octet completion is the determining factor in the lability of all other elements attached to the nucleus. In other words, a labile hydrogen is attached to a negative carbon atom, while a labile radicle other than hydrogen is attached to a positive carbon.

Thus, any rule which expresses the facts of substitution will be reversed in the case of replacement; by "reversed" we mean that a group which causes *substitution* in the meta position will favour *replacement* in the ortho-para positions, and conversely.

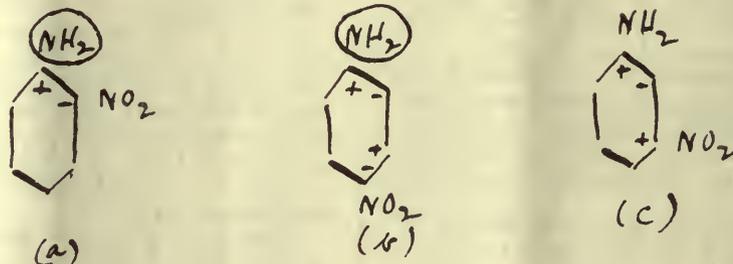


Fig. 4.\*

For example, the nitro group causes substitution in the meta position; but in the hydrolysis of the nitranilines, replacement of  $\text{NH}_2$  by  $\text{OH}$  occurs at the ortho-para positions to the nitro group, and not at the meta position. Reasoning on the same lines as those employed in the discussion of substitution, it will be seen (Fig. 4, a and b), that the octet stability of  $\text{NH}_2$  is reinforced by the polarity effects of the nitro group: whereas in Fig. 4 (c), the polar tendencies of  $\text{NH}_2$  and  $\text{NO}_2$  are opposed, and the lability of  $\text{NH}_2$  consequently diminished.† We have found the above rule (which is, of course, the obverse of the Brown and Gib-

\* A ringed group, thus  $\text{(x)}$ , is used here to denote lability following on octet stability.

† Reference to Case VI. shows that nitraniline exists as two electromers, the  $\text{NH}_2$  group exerting the greater directive influence. It would appear that the lability of a group is more easily influenced by one of opposite polar tendency than is its directive influence; and this is in general agreement with our views on reactivity. In this connection it should be noted that the  $\text{NH}_2$  group in aniline itself, while exerting full directive power, requires the reinforcement of ortho or para nitro groups to render it labile in hydrolysis; and many other similar instances could be cited.

son rule) to be of general application to the simpler cases.

Another interesting rule follows from the unique electrical character of the carbon atom discussed above, if we enquire how the tendency there mentioned towards increasing differentiation of polarity in a chain of carbon atoms can be satisfied. § The inductive effect of a substituent on the carbon atoms of the nucleus is greater the greater its octet stability (*cf.* discussion of the Holleman Series); hence the differentiation of polarity of the carbon atoms will be increased by the replacement of the given substituent by a group of greater octet stability. The rule may therefore be stated thus; in replacements, *the entering group is one of greater octet stability than the group replaced.* The hydrolysis of the nitriles is a case in point, and many others have been examined, and the rule found to hold.\*

A striking example of the application of the rule is seen in the work of Swarts (*Bull. Acad. roy. Belg.*, 1920, 389) on the nature of the  $CF_3$  group.  $CF_3$  is, as one would expect, meta directive. Unlike  $C_6H_5CCl_3$ ,  $C_6H_5CF_3$  can be nitrated under ordinary conditions without hydrolysis of the  $CF_3$  group. This is precisely what we should expect on the octet view. It was pointed out (see last week's issue) that fluorine was in all probability more octet stable than any other atom or group; therefore, while the replacement of Cl by the more octet stable OH group is to

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§ *The rules of Michael and Markownikoff may be a consequence of this property of a chain of carbon atoms, the inductive effects being more pronounced when the chain is unsaturated (Kermack and Robinson, loc. cit., pp. 430-432). In the examples  $CH_2=CH\cdot COOH + HBr = BrCH_2\cdot CH_2\cdot COOH$ ; and  $CH_3\cdot CBr\cdot CH_2 + HBr = CH_3\cdot CBr\cdot CH_3$ , the reaction has taken place which increases the polarity (positive or negative) of the carbon atoms.*

\* An apparent exception to the rule is the action of  $PCl_5$  on phenols, where OH is replaced by Cl. The chlorines in  $PCl_5$ , however, may be in an exceptional state of octet stability (*cf.* Thomson, *Phil. Mag.*, 1921, [vi.], XLII., 521). It is in agreement with the deductions above that the reaction takes place more readily with *p*-nitrophenol than with phenol itself.

be looked for, replacement of F by OH is, according to the rule, difficult or impossible.

Hitherto the application of the rule has been confined to the entry of groups of an essentially electronegative character; but we have found that the important class of reduction reactions, where a group is replaced by hydrogen, falls equally under the rule. In a recent series of papers, Macbeth and his co-workers (Henderson and Macbeth, *T.*, 1922, CXXI., 892; Hirst and Macbeth, *ibid.*, p. 904; Macbeth, *ibid.*, p. 1116) have pointed out that, different as are the structures of compounds with halogens labile towards reducing agents, they have in common the possession of halogen with a strong induced positive polarity—that is, on our view, octet unstable. The octet instability in the cases cited by these authors appears to be unusually pronounced, and hence their ready replacement by negative (octet stable) groups is not to be expected. Their replacement by hydrogen, however, which tends to become electropositive and "octet stable" at the same time (*vide supra*), is in agreement with the rule and with its underlying foundation, *viz.*, *the tendency towards increasing differentiation of polarity of the carbon atoms.* The replacement of the halogen by metals in this class of compound (Henderson and Macbeth, *loc. cit.* p. 895) is a similar example of the rule.\*

It is important to note here the finding of Burton and Kenner (*T.*, 1922, CXXI., 675), that in the removal of halogen in the reduction of halogenated nitro-compounds, the reduction of the nitro groups to amino groups in all probability precedes the removal of the halogen (*cf.* the examples cited by Burton and Kenner, *loc. cit.*, and the papers of Macbeth and his co-workers mentioned above). The present theory would predict that such is the course of these reactions.

#### EFFECT OF GROUPS ON EACH OTHERS REACTIVITY.

We can now refer more particularly to the loosening or tightening effects on substituents caused by other groups present in the nucleus, as has been referred to already

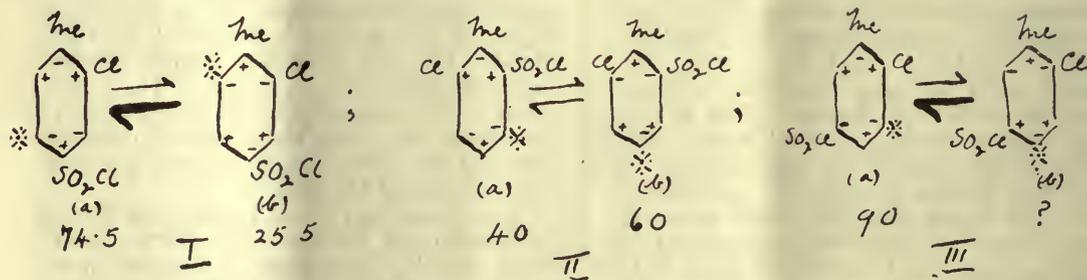
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\* *The activity or inertness of halogen in the compounds cited by Kenner (T., 1914, CV., 2719) and explained by him on Flürscheim's formulation, can be equally well interpreted, along the above lines, on our views.*

in the simpler cases (Fig. 4). Among the numerous examples examined, may be cited the following: the loosening effect of meta directive groups on substituents in the ortho-para positions (Schopf and his collaborators, *Ber.*, 1889, XXII., 900, *et seq.*; Kenner, *loc. cit.*); the loosening of ortho-para directive groups on substituents in the meta position (Kenner and Parkin, *T.*, 1920, CXXVII., 855; Holleman and Hollander, *Rec. trav. chim.*, 1920, XXXIX., 435; Guia, *Gazzetta*, 1921, LI., i., 307; Burton and Kenner, *T.*, 1922, CXXI., 489); the tightening effect of ortho-para directive groups on bromine in the para position (Meyer, *Ber.*, 1921, LIV., [B], 2265). An examination of these will show that our views, and in particular Postulate 3, are capable of predicting the observed facts.

#### THE DIRECTING GROUP IN POLYSUBSTITUTED COMPOUNDS.

In a large number of cases examined by



Percentage yield of corresponding nitro compounds (substitution at asterisk).

Fig. 5.

The substances on which Davies worked (Fig. 5) contain in each case  $\text{CH}_3$  and  $\text{Cl}$  in the ortho relation, the  $\text{SO}_2\text{Cl}$  occupying various positions relative to them. The octet stability of  $\text{Cl}$  being greater than that of  $\text{CH}_3$ , the predominating polar state of the molecule, in the absence of the  $\text{SO}_2\text{Cl}$  group would be as indicated in Fig. 5, ia, iia, iiii. Consider now the question of the persistence of induction. In Fig. 5 i., the inductive tendency of  $\text{Cl}$  in reversing the natural polarity of  $\text{SO}_2\text{Cl}$  is greater than that of  $\text{CH}_3$ , which has the opposite tendency, owing to the difference in the number of carbon atoms through which induction has to be effected. On the other hand,

Robinson (Perkin and Robinson, *T.*, 1914, CV., 2379; Jones and Robinson, *T.*, 1917, CXI., 906; Gibson, Simonsen, and Rau, *T.*, 1917, CXI., 73), it is found that when a negative group is in the ortho-para position to a positive group, they neutralise each other, and the orientating effect is exercised by the second positive group. The work of Davies on the cumulative effect of the chlorine atom and the methyl and sulphonyl chloride groups on substitution (Davies, *T.*, 1921, CXIX., 853-876; *ibid.*, 1922, CXXI., 785) affords interesting examples of the applicability and otherwise of the Robinson rule.

In attempting to determine the position taken up by a fourth substituent in a tri-substituted derivative, two main considerations are of importance, viz., the relative octet stabilities of substituents already present, and the persistence of their inductive effects through a chain of carbon atoms.

in Fig. 5 ii., the greater inductive power of  $\text{Cl}$  as compared with  $\text{CH}_3$  is balanced by the weakening effect of the carbon atoms intervening between  $\text{Cl}$  and  $\text{SO}_2\text{Cl}$ .\* In Fig. 5 iii., the  $\text{SO}_2\text{Cl}$  and  $\text{Cl}$  have the same polar effects on the nuclear atoms. The

\* Morgan and Jones (*T.*, 1921, CXIX., 187) on nitrating 2-chloro 6-nitrotoluene, obtained 90 per cent. of the compound corresponding to iia above, and 5-10 per cent. of iib. Reference to remarks on the order of the meta directive substituents indicates that electromer (i) can exist in greater concentration when an  $\text{NO}_2$  group is in place of  $\text{SO}_2\text{Cl}$ .

electromeric equilibria in the three cases will therefore be as shown in that figure, and the yields of the nitration products are in agreement. Thus it will be seen that the present theory is borne out by the above experiments; whereas the Robinson rule fails in the third example (*v.*, Davies, *T.*, 1922, CXXI., 786; but compare footnote to same page).

The results of Gibson, Simonsen, and Rau (*T.*, 1917, CXI., 69) on the nitration of 2-acetylamino-3-4-dimethoxybenzoic acid and of 3-acetylamino-veratrole, and of Simonsen and Rau (*T.*, 1917, CXI., 220) on the nitration of isomeric acetylamino methoxybenzoic acids, are difficult of interpretation on the octet view, partly owing to the large number of substituents, and hence the difficulty of determining their mutual interdependence; and partly to the difficulty at the present stage of dogmatising with regard to the relative octet stabilities of NHAc and OMe.

In the above, we have attempted, on the basis of the Thomson-Lewis-Langmuir theory of co-valence, to connect various theories and rules which at first sight may seem wide apart; to give as consistent a basis as we could to certain observed regularities; and further, to formulate generalisations which may be of use in classifying, and perhaps in predicting the course of, substitution reactions.

#### SUPPLEMENTARY NOTE.

It should be observed that our view of the mechanism of induction differs somewhat from that of Kermack and Robinson (*loc. cit.*), inasmuch as actual "appropriation" of electrons by octet stable centres is postulated by us. That this is not the opinion of Kermack and Robinson was made clear by Professor Robinson at the Hull meeting of the British Association, 1922. It is our intention to attempt to obtain experimental evidence, which will give at least a pointer as to the correctness or otherwise of our ideas on this point.

*Chemistry Department,  
University of Aberdeen.*

#### A NEW TEST FOR NITRATES.

By IVOR G. NIXON.

The "Ring Test" for nitrates possesses two main disadvantages, namely, the ferrous sulphate solution does not keep well,

whilst if made up freshly each time, the salt dissolves but slowly in the cold water. It appeared possible to the writer that some of the nitro-sulphonic acids of the naphthalene series, which are noted for their intense and persistent yellow or red colour in solution, might be utilised to provide a sensitive test for nitrates which would be free from these disadvantages. These nitro acids are easily formed by adding nitric acid to a solution of the sulphonic acid in concentrated sulphuric acid, hence it would appear possible that the addition of a few drops of a water solution of one of these sulphonic acids to a mixture of the suspected nitrate, in water solution, with an excess of concentrated sulphuric acid, should cause a distinctive colour to be developed if a nitrate is present. This test was tried, using  $\beta$ -naphthalene sulphonic acid, but negative results were obtained. "G Salt" (2:6:8 naphthol disulphonic acid), "Gamma acid" (2:6:8 aminonaphthol sulphonic acid), "Schaffer's acid" (2:6 naphthol sulphonic acid), and the "Cleve's" acids (1:6 and 1:7 naphthylamine sulphonic acids), however, were all found to react vigorously, giving wine red solutions. The test is very sensitive, with "G Salt," for instance a distinct red colour is given by 0.02 milligrams of nitrogen as nitric acid, whilst with much smaller quantities a faint yellow colour is still obtained. Under these conditions, the "Ring Test" gives negative results. There is no need to cool the solutions during the test, as must be done during the ring test. Indeed, it was found that the application of moderate heat often deepens the colour—thus if the test mixture in which "G Salt" has been used is boiled, the colour becomes more intense, and rather bluer in tone. Under the same conditions for "Gamma acid," the wine red colour of the solution becomes an olive-green. Nitrites also answer to the test. The general method of procedure is as follows:—

About one cubic centimetre of the suspected solution is mixed with approximately an equal volume of concentrated sulphuric acid, and then about five cubic centimetres of a 1 per. cent. solution of "G Salt" slowly added, if a nitrate or nitrite is present an intense wine red colour is developed. The test may also be applied as a ring test, in this case, the nitrate solution is mixed with that of the sulphonic acid, and concentrated sulphuric acid then run

down the side of the test tube. A red ring is formed at the junction of the two liquids, and on shaking the tube, this colour is communicated to the whole of its contents.

## AN EXPLANATION OF THE THEORY OF THE ROTATION OF THE ATOMIC NUCLEUS.

By Herbert Henstock,

### PART I.

In a previous communication (*The Chemical News*, 1923, CXXVI., 129) the author gave a general description of the manner, in which the atomic nucleus plays its part in the union of atoms, together with certain effects and consequences which must follow such action. It is now proposed to describe this action a little more in detail, and to attempt to show its bearing upon some of the difficulties met with both in inorganic and organic chemistry: but before showing its applications to concrete cases, it has been thought better to give a general explanation here, and to defer particularisations to the future parts of this series.

This hypothesis in no sense pretends to supersede or to invalidate the theory of the Induced Alternate Polarity of Atoms, but is put forward as an explanation of the underlying cause of that theory, or, to be more exact, that law; for alternate polarity has now got beyond the stage of theory and is beginning to be recognised as an actuality. In explanations of alternate polarity, as, for example, that given by Kermack and Robinson (*Trans. Chem. Soc.*, 1922, CXXI., 427), the idea that a negative atom appropriates to itself some of the electrons of neighbouring atoms, and that a positive atom tends to disintegrate, may or may not be true; but the author's point is that all such features are merely manifestations or results of alternate polarity and not the cause of it, the cause is the nucleus of an atom.

If this hypothesis be applied to the Lewis-Langmuir conception of the atom, then the general effect of the nucleus upon the octet will be seen from Fig. 1.

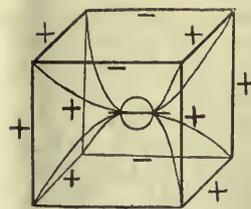


Fig. 1.

Part of the number of edges, where single valence bonds may exist, will be positive and part negative in the same atom, so that when two atoms of the same element unite to form a molecule they both have similar potentialities for molecule formation. If we imagine such an atom travelling with one of its negative edges in front, when it meets another atom similarly situated moving to meet it, the second atom will probably rotate as a whole until one of its positive edges faces the first atom, when union will occur: this will be especially the case in those elements strong in "permanent polarity" (*The Chemical News*, loc. cit.), but it is more than probable that this will occur between all atoms of the same element. The case may be somewhat different, however, between two or more atoms of different elements: an atom, strong in permanent polarity, may actually rotate the nucleus of another much weaker one; as an example, a chlorine atom may rotate the nucleus of a carbon atom, but would not rotate that of a sodium atom, the sodium atom would rotate as a whole till a positive edge faced the chlorine, just as would be the case with two chlorine or two sodium atoms. This effect may be seen from Fig. 2.

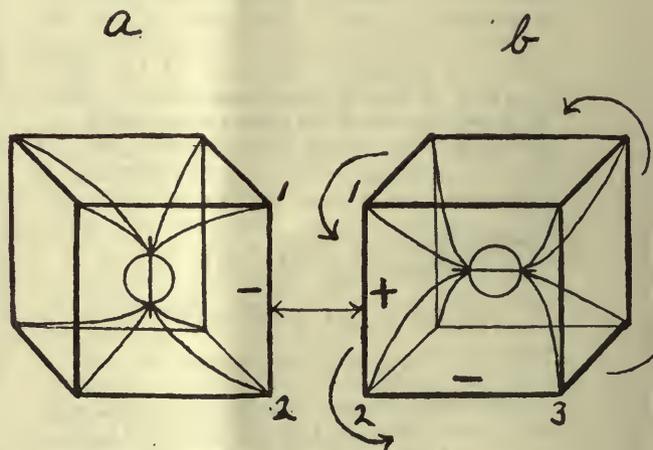


Fig. II.

If A and B be two chlorine atoms, and A is travelling towards B with its edge 1-2 in front, and B is moving towards A with its edge 2-3 in front, then the whole of atom B will revolve till its edge 1-2 faces A. If A be a chlorine and B a sodium atom the same thing will happen, but if A were a chlorine and B a carbon atom, then the union might be made between A 1-2 and B 2-3, but the nucleus of B would revolve through an angle of  $90^\circ$ , making the edge 2-3 a positive one, especially if the carbon atom were already combined with other atoms.

In working out the various problems, the following rules have been found to hold good:—

(1) The normal primary valencies in any atom will be wholly confined to negative or wholly to positive edges.

(2) When an atom unites normally by its negative edges and any compound is formed where a positive edge comes into play, then that compound will be an unstable one. The converse for normal positive edges also holds.

(3) The nearer together the nuclei come in a molecule, the more unstable it will be.

(4) Electrons are more strongly held to the nucleus along a negative edge than along a positive one.

(5) When electrons are moved from one corner to another in the octet, a strain is caused in the atom.

(6) Two electrons at one corner in a bond are a source of weakness in the bond.

(7) Distortion of the octet is always a source of weakness in the molecule.

A chain of atoms will be represented as in Fig. 3.

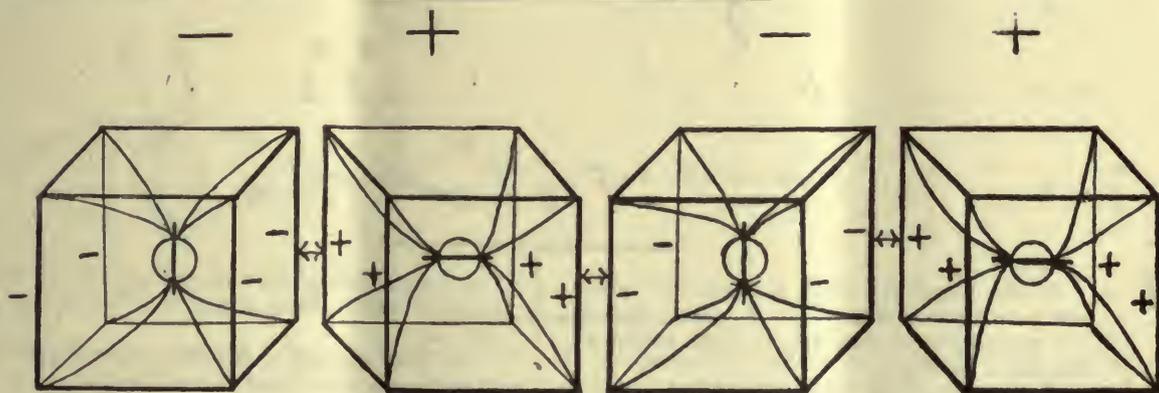


Fig III

The normal unsatisfied valence bonds will lie in the vertical direction in each atom in accordance with rule (1), and any union along a horizontal bond will be unstable, as follows from rule (2).

Lapworth's law of alternate polarities is here clearly demonstrated.

A double bond is shown in Fig. 4.

The two cube faces both come together, so that four edges touch in each atom, which constitutes one of the weaknesses of the double bond, since in the case of the negative atom rules (1) and (2) both operate. Also the nuclei are nearer to

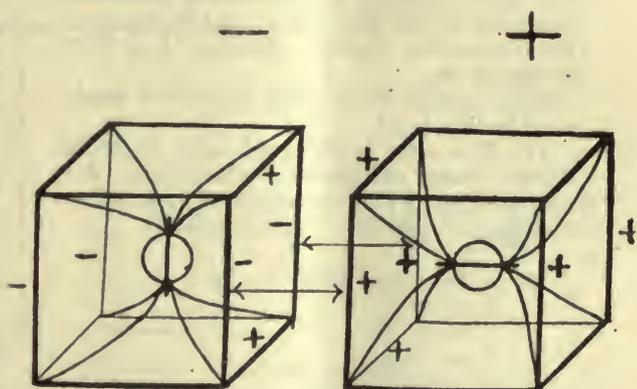


Fig IV





Distortion of the octet must occur in a double bond, and there seems no reason why it should not do so in all atoms where there are three or four vacant corners to the cube; in fact, some kind of distortion might occur in any uncombined atom, with the exception of those of the inert gases. It is inconceivable to imagine that the element carbon alone has the form of what might be termed a distorted cube. In the case of carbon this distortion may occur not only to the extent of the complete tetrahedron but, as will be shown later, partial distortion of the cube, between it and the tetrahedron may occur when carbon is in the combined state. This idea may be extended to the octets of the other elements, and in

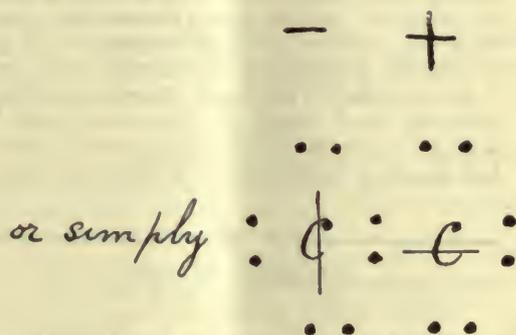
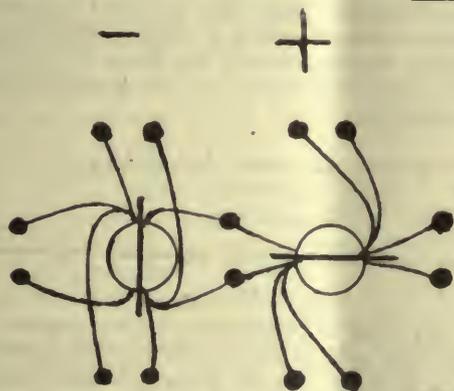
conjunction with the direction of the tubes of force emanating from the nucleus it will be found capable of explaining many anomalous cases of valence, together with weakness in bonds with consequent instability of molecules.

The usual notation suffices to show the arrangement of electrons and bonds, if it be remembered that all the ordinary unions are made normally

I.—By single bonds:

(a) In negative atoms by electrons which are joined to opposite ends of the nucleus.

(b) In positive atoms by electrons which are joined to the same end of the nucleus.



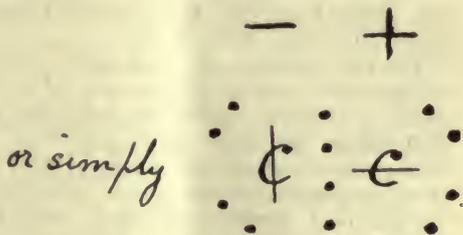
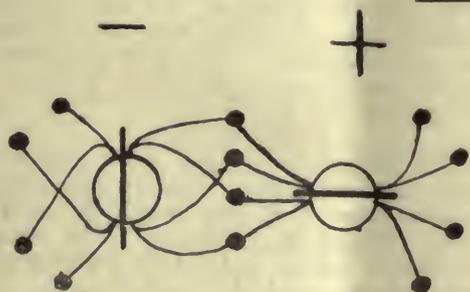
In each of the pairs, the electrons are to be imagined to be one above the other in planes at right angles to the plane of the paper, and *not* in the plane of the paper: this also applies to double and treble bonds.

II.—By double bonds:

(a) In negative atoms the four electrons of the double bond are alternately

joined to either end of the nucleus and in the remaining two unions the electrons of each pair are joined to opposite ends of the nucleus.

(b) In positive atoms double bond electron pairs are joined to one end of the nucleus, the other two valence pairs to the opposite end.



III.—By treble bonds:

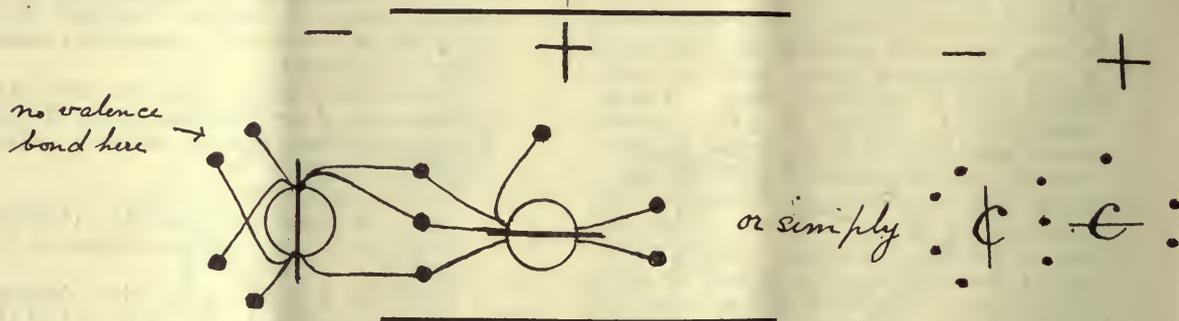
(a) In negative atoms the three electrons, forming the bond, are joined two to one end of the nucleus and one to the

other; the two electrons forming the single bond are each joined to opposite ends.

(b) In positive atoms all three electrons

of the treble bond are joined to one end of the nucleus, and the two single bond

electrons to the other end.



Here it cannot be seen that the positive carbon atom shares two of its electrons with the negative, which latter shares but one with the positive, without reference to Fig. 5. In the negative atom there is only one "single bond," although there are four electrons, and in the positive atom there is a single electron which is apparently alone, but the true significance is not seen with-

out drawing the octets and putting in the lines of force, when the matter at once becomes clear, which is a good demonstration of the importance of the lines of force in any cases of doubt as to how a substance is constituted.

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## GENERAL NOTES.

### GERMANY'S TRADE INDUSTRY DURING MARCH.

The Commercial Secretary at Berlin (Mr. J. W. F. Thelwall) has forwarded to the Department of Overseas Trade a survey of the position of trade and industry during March.

It appears that un-occupied Germany has borne the cutting off of her most important industrial area comparatively well. The anticipated shortage of coal has not set in. The demand for pig iron and steel was also met. This was possible owing to the existing stocks, and increased imports, especially of English coal.

In the textile and tobacco industries there were further indications of a retrograde movement, while employment in the remaining industries was generally satisfactory in spite of high costs of production in consequence of the use of English coal. In occupied territory, however, works were compelled to incur heavy unproductive expenditure, and their free development was greatly interrupted by the blockade and other acts of intervention by the occupying Powers. They were forced to continue to work for stock.

### Mining.

No definite information with regard to the coal output of the Rhenish-Westphalian coal district can be given. In the Central German brown coal district a not inconsiderable increase of output occurred. There was, however, an interruption of sales owing to a smaller demand on the part of the sugar working-up industry and also of the potash industry. The demand for Upper Silesian coal also partly ceased. It thus appeared that buyers had quickly covered their requirements as a result of the Ruhr occupation, and, with the uncertain economic situation and the expected reduction of coal prices, were not yet ready for new purchases. The gasworks belonging to communities particularly showed reserve in placing new orders.

### Potash Industry.

The market conditions were unfavourable. In particular German agriculture, whose demand in this month is usually great, limited its purchases. The reason for this lay partly in the high prices of potash and coal, and also high freights, and partly because German farmers covered their requirements sufficiently in previous months at cheaper potash prices and freights. Foreign trade was confined with-

in comparatively narrow limits: only for sulphate of potash salts was the demand satisfactory. The market for the by-products of the potash industry also left much to be desired.

The *aluminium industry* continued to suffer, and the outlook for the near future is bad.

The *electro-technical industry* also suffered from lack of orders. An ample demand for electrical plant of all kinds existed, but there was nowhere any possibility of raising the requisite capital.

In general, employment in the electro-technical industry is assured for months ahead.

#### *Chemical Industry.*

Owing to the fact that prices in the chemical industry had reached and partly exceeded the world's market level, foreign orders declined. Competition with foreign countries was rendered particularly difficult by high railway freights, postal fees, and coal prices. In expectation of a reduction of prices, inland customers covered only their immediate needs in small quantities. There was still in stock a heavy proportion of goods purchased at high prices in January and February which could be disposed of only at a loss. Business in chemically pure reagents and preparations was almost completely at a standstill, owing partly to the closing of all institutes and universities for Easter.

#### *Indiarubber Industry.*

The position was unsatisfactory. The shortage of German coal necessitated increased purchases of English fuel. Conditions on the inland market were thoroughly unfavourable.

#### *Glass Industry.*

In the sheet glass industry the supply of raw materials was, in general satisfactory. The costs of manufacture approached the world's market prices. The inland demand continued to fall off. Belgian and Czech glass industries greatly injured the German industry on foreign markets, so that only very few sales to the eastern Border States were possible. Exports to Italy, Africa, and America were small. In the hollow glass industry a stagnation of sales set in, resulting in restrictions of work."

#### *Fertilisers.*

The market for nitrogenous fertilisers was stagnant. Some factories in occupied territory had to cease work. Prices were such that German nitrogen was still cheaper than foreign nitrogen.

In order to afford farmers who have not yet placed their spring orders, the possibility of purchasing nitrogenous fertilisers cheaply, the Nitrogen Syndicate has decided to sell such fertilisers for the time being at reduced prices, quite out of proportion to the reduction in coal prices of the 1st April. The lowered prices came into effect on the 3rd April.

#### SCIENTIFIC APPARATUS FOR BRITISH COLUMBIA.

H.M. Trade Commissioner in Vancouver, British Columbia (Mr. L. B. Beale) reports that the authorities of the University of British Columbia are desirous of receiving from U.K. manufacturers illustrated catalogues, full particulars, and prices of scientific apparatus.

Further particulars, together with the names of the enquirers, may be obtained by firms interested upon application.

The Commercial Secretary at Bucarest reports that the Roumanian Railroad Administration invites tenders for the supply of sulphate of copper.

Application for particulars should be made to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.

#### THE DYE INDUSTRY.

##### NEW CAREERS CREATED BY AN ACT OF PARLIAMENT.

The effect upon the career of University men of new conditions in the Dyestuffs Industry is discussed in an interview by Professor Arthur G. Perkin, F.R.S., the head of the Departments of Colour Chemistry and Dyeing at Leeds University, where the summer term has just opened.

"Although the number of students entering our Colour Chemistry and Dyeing Department is falling, he said, "it still remains much higher than at any time before the war. A decrease to some extent is inevitable because, in the first place, many ex-army men have now finished their training, and, at the same time, fees have of necessity been considerably increased. This, I am afraid, may prevent many young men from taking our course.

"In the future we may have a normal sixty students taking our three years'

course either for the Diploma or Ordinary B.Sc. in dyeing, or our four years' course, leading to the Honours B.Sc. in colour chemistry. In this case some twenty students will enter the dyeing, colour chemistry and allied industries each year. Much, however, depends upon Government action; for, if they repeal the Dyestuffs Act, there is no doubt that the artificial dyes industry will become moribund in this country. As it is, the forty-seven students who left me this year have all obtained positions not only in colour works, but in wool dyeing, cotton dyeing, calico printing, artificial silk, and other industries."

### THE MINERAL OUTPUT OF YUKON.

Figures are to hand, authenticated by the District Gold Commissioner, Mr. George P. MacKenzie, showing the output of gold, silver, lead, and copper from this territory. The dominant note in his report is one of sheer optimism that the future holds much good, in the productive sense.

Conservative quotations show the total output as follows: Gold, \$200,000,000; silver, 3,500,000 ozs., valued at \$2,100,000; lead, 3,500 tons, valued at \$400,000; copper, 12,000,000 pounds, valued at \$2,700,000. Two million ounces of the silver was produced as a by-product in refining placer-gold; and the Mayo district, so long unworkable owing to difficulties of transport, has so far developed that 1,500 claims are now staked.

It has long been feared in the circles concerned that the mines were becoming used up, and that very little metal remains. Mr. MacKenzie refutes this belief, and terminates an interesting report with the following paragraph:—

"The views of the residents of the territory and all those interested in its mineral resources and production are now most optimistic. The life of the placer fields is anything but over, and now it appears certain that a period during which the silver-lead areas of the territory will equal or exceed the gold fields in the production of wealth has just been entered upon, while further gold, silver, and copper deposits may be said to be held in reserve awaiting the day when the world market calls them."

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### THE ROYAL SOCIETY.

THURSDAY, APRIL 26.

Papers read:—

T. R. MERTON, F.R.S., and R. C. JOHNSON: *On Spectra associated with Carbon.*

R. A. WATSON WATT and E. V. APPLETON, D.Sc.: *On the Nature of Atmospherics.* Communicated by Sir Henry Jackson, F.R.S.

W. A. BONE, F.R.S., D. M. NEWITT, and D. T. A. TOWNEND: *Gaseous Combustion at High Pressures. Part III.: The Energy absorbing Function and Activation of Nitrogen in the Combustion of Carbon Monoxide.*

I. MASSON, D.Sc., and L. G. F. DOLLEY: *The Pressures of Gaseous Mixtures.* Communicated by Professor F. G. Donnan, F.R.S.

Papers read in title only:—

W. R. BOUSFIELD, F.R.S., and C. ELSPETH BOUSFIELD: *Vapour Pressure and Density of Sodium Chloride Solutions.*

F. A. LINDEMANN, F.R.S., and G. M. B. DOBSON: *A Note on the Temperature of the Air at Great Heights.*

G. H. HARDY, F.R.S., and J. E. LITTLEWOOD, F.R.S.: *On Lindelof's Hypothesis concerning the Riemann Zeta-function.*

#### ROYAL INSTITUTION.

On Thursday, April 26, Professor J. T. MACGREGOR-MORRIS began a course of three lectures at the Royal Institution on *Modern Electric Lamps*. On Saturday, April 28, Dr. LEONARD WILLIAMS will deliver the first of two lectures on the *Physical and Physiological Foundations of Character*.

The Friday evening discourse on April 27 will be delivered by Mr. C. V. BOYS, on *Measurement of the Heating Value of Gas*, and on May 4 by PROFESSOR SODDY, on the *Origins of the Conception of Isotopes*.

#### ROYAL SOCIETY OF ARTS.

On Friday, April 20, there was a joint meeting of the Dominions and Colonies and the Indian Sections. SIR RICHARD A. S.

REDMAYNE, K.C.B., M.Sc., M.INST.C.E., M.I.M.E., F.G.S., delivered a lecture entitled *A Review of the Base Metal Industry, with Special Reference to the Resources of the British Empire*. The Rt. Hon. Lord Emmott, G.C.M.G., G.B.E., presided.

On Monday, April 23, MR. E. KILBURN SCOTT, M.I.E.E., A.M.INST.C.E., gave his (third) Cantor lecture, *Nitrates from Air*.

On Wednesday, April 25, there was a conference on *The Milk Question* at the Ordinary Meeting. Short papers were read as follows: (1) *The Arguments for Maintaining an Open Market for Fresh Milk*, by PROFESSOR R. STENHOUSE WILLIAMS, M.B., B.Sc., L.R.C.P., and S.E., D.P.H.; *Changes in the Digestibility and Nutritive Value of Milk Induced by Heating*, by PROFESSOR J. CECIL DRUMMOND, D.Sc., F.I.C.; (3) *The Effect of Heat on Some Physiological Principles in Milk*, by S. S. ZILVA, Ph.D., D.Sc., F.I.C. A demonstration of some of the chemical changes in milk on heating to various temperatures was given by CAPTAIN JOHN GOLDING, D.S.O., F.I.C., and MRS. A. T. R. MATTICK, M.Sc. The Rt. Hon. F. D. Acland, M.P., presided.

#### ARRANGEMENTS FOR MEETINGS UNTIL THE END OF THE PRESENT SEASON.

Monday, April 30, 8 p.m. (Howard Lecture): *The Development of the Steam Turbine*, by STANLEY S. COOK (Lecture 1).

Wednesday, May 2, 8 p.m. (Ordinary Meeting): MAURICE DRAKE, *The Fourteenth Century Revolution in Glass Painting*. Professor W. R. Lethaby will preside.

Monday, May 7, 8 p.m. (Howard Lecture): *The Development of the Steam Turbine*, by STANLEY S. COOK (Lecture 2).

Wednesday, May 9, 8 p.m. (Ordinary Meeting): WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S., Professor of Chemical Technology, Imperial College of Science and Technology, South Kensington. *Recent Developments in Surface Combustion*. D. Milne Watson M.A., LL.B., Governor of the Gas Light and Coke Company, will preside.

Monday, May 14, 8 p.m. (Howard Lecture): *The Development of the Steam Turbine*, by STANLEY S. COOK (Lecture 3).

Wednesday, May 30, 4.30 p.m. (Ordinary Meeting): A. J. SEWELL, *The History and Development of the Perambulator and Invalid Carriage*.

Friday, June 1, 4.30 p.m. (Indian Sec-

tion): AUSTIN KENDALL, I.C.S. retd., *The Indian Section of the British Empire Exhibition, 1924*.

Friday, June 15, 4.30 p.m. (Indian Section): SIR JOHN H. MARSHALL, C.I.E., M.A., Litt.D., F.S.A., Director-General of Archaeology in India, *The Influence of Race on Early Indian Art*. (Sir George Birdwood Memorial Lecture.)

#### ROYAL MICROSCOPICAL SOCIETY.

The section of the Society which has been formed to deal with the Industrial Applications of the Microscope, and to assist in the development of Industrial Research in British Industries, held a meeting on Wednesday, April 25.

Messrs. C. Baker exhibited their junior engineer metallurgical microscope and the Greenough binocular microscope.

Messrs. R. & J. Beck, Ltd., demonstrated a new research outfit for metallurgical work, including microscope, camera, optical bench, etc.

The Edison Swan Electric Co., Ltd., showed their projector and fullolite lamps.

Mr. Mansell P. Swift demonstrated the use of Dichroscopes for the identification of certain gem stones.

Messrs. W. Watson & Sons exhibited petrological microscopes.

Mr. J. E. BARNARD, F.INST.P., F.R.M.S. gave the first of a series of short communications on *The Manipulation of the Microscope in Industrial Laboratories*. Part I.: *Illuminants and Illumination*.

DR. MARIE C. STOPES, D.Sc., Ph.D., F.L.S., read a paper entitled *The Microscopical Examination of Coal in relation to Fuel Economy and Efficiency*.

Future meetings will be held as follows:

May 16: MR. LEONARD TAVERNER, A.R.S.M., *The Principles and Application of Technical Metallurgical Microscopy*.

MR. W. M. AMES, M.A., B.Sc., A.I.C., *Applications of the Microscope in the Manufacture of Rubber*.

May 30: MR. JOSEPH M. COON, *On the Microscopical Determination of Cassiterite in Rock Sections*.

MR. H. B. MILNER, *The Microscopical Investigation of Sands for various Industrial Purposes*.

The Industrial Applications Section of the Royal Microscopical Society has been formed for the purpose of assisting in the

development of Industrial Research in British Industries, and holds regular monthly meetings with practical demonstrations connected with the reading and discussion of communications dealing with Industrial Research problems.

Enquiries and suggestions are solicited by the Honorary Secretaries to the Section: W. E. Watson Baker, A.Inst.P., 313, High Holborn, W.C.1, C. F. Hill, M.Inst.M.M., A.Inst.P., Moore, Warrington.

#### THE CHEMICAL SOCIETY OF JAPAN.

The following papers have been communicated to the Society:—

*Studies on Accelerators of Oxidation.* Part I. *Action of Ferric Sulphate upon Potassium Permanganate*, by BUNSUKE SUZUKI and CHUJIRZ HAMADA.

*On the Oxidase-like Action of Complex Salts of Metals.* Part III. *Decomposition of Hydrogen Peroxide by Complex Salts of KANEKO.*

*Influence of Heating and Oxidation on the Vitamine A and B of Milk*, by HIDE-SABURO SEKINE and TAMOTSU OKAMURA.

*Studies of Metallic Oxides and their Hydrates by X-Rays.* Part I. *X-Ray Analysis of Stannic Oxide and its Hydrates*, by NOBUO YAMADA.

*Braun's Law and Thallous Sulphate*, by FUSAO ISHIKAWA.

The Society of Motor Manufacturers and Traders, Ltd., have decided to organise, from Thursday, November 22, to Saturday, December 1, 1923, in the recently enlarged Olympia, an Exhibition embracing not only the various types of commercial motor vehicles and their components and accessories, but also plant, machinery and materials used in the construction, maintenance, and development of roads.

The exhibition will be divided into four sections: Commercial motor vehicles and body work; accessories and components; tyres; and road plant, machinery, and materials.

The exhibition manager will be pleased to supply copies of the conditions and forms of application for space, on application to the Society's offices, 83, Pall Mall, London, S.W.1.

#### CORRESPONDENCE.

##### ATOMIC THEORIES.

*To the Editor of THE CHEMICAL NEWS.*

SIR, — With regard to the notice of the second edition of my *Atomic Theories*, which you kindly gave in your last issue, the point raised by the reviewer concerning the positions of the electrons in the carbon atom is certainly an interesting one.

At the time of writing I did not regard the positions of the electrons as absolutely assigned and always definitely fixed to certain corners of the cube; for, even supposing the arrangement to be as shown by Fig. 19, on page 90, which is the one expected when the four electrons are free to take up positions of equilibrium in the outer shell of the atom. But in the case of the combination shown in Fig. 33 on page 90, it seems probable, as your reviewer has pointed out, that the electrons might take up changed positions to meet the vacant places in one of the oxygen atoms, if this latter happens to be in the position shown in the figure.

If, however, one of the oxygen atoms is orientated through an angle of 90 degrees, then, of course, this orientation of the carbon electrons would not take place. The electrons would have the positions as shown in the earlier figure.

Other considerations also tend to show that the electrons may alter their positions in the atoms.

I am, Yours, &c.,

F. H. LORING.

London, S.W.4.

April 21, 1923.

#### NOTICES OF BOOKS.

*A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, by J. W. MELLOR, D.Sc. Vol. III., pp. X. + 927. London: Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 1923. Price 63s. net.

This volume covers the elements Cu, Ag, Au, Ca, Sr, and Ba, and the mass of information it contains is enormous. Each element is dealt with from historical, geological, physiological and purely chemical aspects, and the various derivatives are enumerated separately. The last three substances are collected under the heading of alkaline earths.

There is no doubt that the work covers every by-way in the scientific knowledge of the elements, and the time and labour spent upon it cannot be described otherwise than as colossal; but the author has made the great mistake of adding a profusion of references. For instance, in the chapter upon cupric chloride and the complex salts thereof, there are no fewer than 4 pages of references, with 70 lines to the page.

Considerable attention has been paid to the sources of the elements (*i.e.*, the composition of the ores, etc), their extraction, and alloying. In fact, complete deduction from the crude ore to the most complex B.P. salt is one of the most prominent features. Qualitative and quantitative analyses have been associated with the most up-to-date methods of research, and various theoretical discussions are incorporated with great thoroughness.

Efficiency in authorship and editorship is evident in its maximum degree, and the work is most valuable for complete reference. So far, it is incomplete, further volumes being in preparation, the next one dealing mainly with the radium and actinium families. We await its publication with interest, and, meanwhile, place the present volume high on the shelves of great works.

J.M.

*Elements of Glass-blowing*, by H. P. WARAN, M.A., Ph.D., F.INST.P. Pp. IX. + 116. London: G. Bell & Sons, Ltd., Portugal Street, W.C.2. 1923. Price 2s. 4d. net.

Manipulative skill in glass-blowing can only be acquired by patient practice—practice, it may be mentioned, along the correct lines.

Students show very unequal capacities in making progress in this direction, whilst much depends on their own ability, expert guidance counts for much. The examples of a clever manipulator greatly help them to become proficient.

The present manual on this subject will be found useful to students and inexperienced research workers called upon to carry out certain glass-blowing work, whether it be merely the joining of two tubes or the making of vacuum tubes or other elaborate apparatus. The principles and advice given by the author are sound, and the illustrations are very clear.

The book should certainly appeal to a wide circle of readers among chemists and physicists.

*Atoms*, by JEAN PERRIN. Authorised translation by D. LL. HAMMICK, M.A. Second English edition revised. Pp. XV. + 231. London: Constable & Co., Ltd., Orange Street, W.C.2. 1923. Price 8s. 6d. net.

The second English translation of Prof. Perrin's *Les Atomes*, which has now been published, has been based upon the eleventh revised French edition.

The contents have been revised where necessary, in accordance with the rapid advances which continue to be made in atomic science.

A particularly lucid account of the experiments and views of Prof. Perrin and others on the Brownian movement, radiation, light and quanta, electrons, etc., are given, together with the advances in the study of the genesis and destruction of atoms by various investigators.

In the section entitled *Appendix*, 1921, there are notes on recent work in certain directions, *e.g.*, Corpuscular Swarms, Bohr's Theory, etc.

This English edition should serve, at least, to make Prof. Perrin's work more widely known, both here and in America.

*Ink*, by C. AINSWORTH MITCHELL, M.A., F.I.C. Pp. VIII. + 128. London: Sir Isaac Pitman & Sons, Ltd., Parker Street, Kingsway, W.C. 1923. Price 3s. net.

Whilst the author has not attempted to compile a laboratory or works manual, he has written a very readable and informative volume, which contains an account of the history and scientific developments of the manufacture and uses of inks.

Sufficient details are given of the processes for preparing the different kinds of ink for ordinary and special purposes, so that a clear and correct impression of the methods may be obtained.

After a description of the raw materials for making iron-gall inks, and their manufacture, there is a chapter on the methods of testing inks in general. In this and other chapters the author's special knowledge and experience is much in evidence. Besides the iron-gall preparations there are now numerous others, *e.g.*, logwood inks, vanadium inks, and those made from aniline black and similar dyestuffs. Special inks, such as those for copying, typewriting and printing, and Indian ink, all receive ade-

quate treatment, consistent with the size of the book.

The information contained in this little volume is noticeably free from industrial and scientific technicalities, thus making it available for general readers, as well as for chemists, analysts and others who may be specially interested in the subject.

*The Recovery of Volatile Solvents*, by C. S. ROBINSON. Pp. 188. New York: The Chemical Catalog Co., 19, East 24th Street. 1922. Price \$2.50.

It is only of late that the recovery of volatile solvents has attained any importance in industrial chemistry. The subject has, however, been well investigated. The author of the present volume, who has himself made valuable contributions on the subject, is of opinion that future improvements in solvent recovery must be principally in the designing of suitable apparatus and in the improved application of known principles.

Prof. Robinson has presented a good and well illustrated account of these fundamental principles and their technical application. The book is divisible into six sections. The first six chapters give the important elementary principles. The technical readers of this volume may find the physical chemistry of this section hard reading, but it is of importance, since the chemical engineering involved rests upon these principles and laws.

The second portion of the book (chapters VII.-XI.) deals with the application of solid absorbents. The third part deals with the recovery of vapours by condensing and cooling processes. Part four (chapter XX.) covers the methods of combined cooling and compression. An account of the various methods of scrubbing constitutes part five, and a long and excellent abstract of the literature constitutes the final section.

This is the first book to deal exclusively with solvent recovery, and the author is to be congratulated upon the care which he has given to the compilation of this valuable contribution to technical literature.



THIS list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Latest Patent Applications.*

- 9004—Chemical Industry in Basle.—Manufacture of soluble acid in calcium salts of inositol-phosphoric acid. March 29.  
 8576—Laporte, Ltd., B.—Manufacture of barium peroxide. March 26.  
 8837—Casselle & Co., Ges.—Manufacture of alkylated derivatives of vat dyestuffs. March 28.  
 8992—Soc. l'Air Liquide, Soc. Anon. pour l'Étude et l'Exploitation Des Procédes G. Claude.—Manufacture of nitrogen peroxide. March 29.  
 8956—Verein für Chemische und Metallurgische Produktion.—Production of chemically pure sulphuric acid. March 29.

*Specifications Published this Week.*

- 194740—Casale, Dr. L.—Process for the synthetic production of ammonia.  
 194709—Waldberg, A.—Electro-metallurgy or the electro-deposition of metals.  
 181677—Blanc, G. A.—Method of and apparatus for the treatment of silicates with acids in order to obtain solutions of salts free from silica.  
 188338—Kinzlberger & Co.—Preparation of iron-free chromium compounds.  
 192941—Phenol-aldehyde condensation products.—Byron, J. G., 1, Norfolk Avenue, Heaton Chapel, near Stockport; and Attwater, R., Hopwood Street Mills, Preston.

Phenol or cresol is condensed with formaldehyde with sodium thiosulphate, or other neutral salt of thiosulphuric acid, as catalyst, thus effecting an economy in formaldehyde, light-coloured products being obtained. In an example sulphur-free cresylic acid is condensed in presence of sodium thiosulphate with formaldehyde which is added in four equal quantities at specified intervals. The product is separated from the aqueous layer and may be diluted with solvents for use as a varnish or may be incorporated with fillers and hardened, for use for example as electrical insulation.

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PAMPHLETS.

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# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3290.

## VALENCY AND RADIATION.

By F. H. LORING.

The octet theory of valency is so satisfactory in most cases as to lead one to conclude that it represents a truth. The Bohr atom, on the other hand, fits in so well with many experimental facts of spectrum analysis that one is compelled to regard this theory as also true in the main; but there is a conflict between these two theories in that the latter, as is well known, involves electrons revolving in planetary orbits round a central sunlike nucleus; while the octet theory, though it in no way necessitates the electrons being at absolute rest, does imply that they cannot circulate in orbits round a central positive nucleus. How, then, are these theories to be reconciled with each other?

Since the Bohr theory is founded on the spectrum of hydrogen, it might be assumed that with one comparatively free electron outside the nucleus, as in the case of the hydrogen atom which is more easily ionised than helium on this account, it would be free to absorb energy and express it potentially in orbital revolution; then give it up as radiation when settling into "stationary" or steady states of revolution in orbits representing less energy, and when this occurrence takes place it involves multiples of energy or quanta  $h\nu$ , where  $h$  is Planck's constant and  $\nu$  is the frequency of the radiation.

When, however, other elements having atoms of more complex structure are considered, difficulties occur both in the Bohr theory and in its reconciliation with the octet theory. These difficulties have been fully realised by chemists and physicists, and several suggestions have been made to meet the difficulties arising therefrom, such, for example, as—

1.—The electrons in their octets vibrating in their mean positions of equilibrium, yet retaining their "corner" positions approximately.

2.—The electrons revolving in small orbits round axes emanating from the corners of the cube.

3.—In the case of helium, the electrons vibrating in semi-circular tracks round a nucleus.

4.—The electrons, in the case of hydrogen only, revolving in circular and elliptical orbits round a nucleus.

Now it will be seen that if these views—taken in a reverse order—are, as it were, plotted, they fall into line, for the first "plot" (4) is a circle or ellipse, the second (3) is a semi-circle, while the third (1) is a more restricted vibration and No. 2 is ruled out. This observation is probably not a significant one, but the transition shown has a good inverse parallel in the three states of matter: solid, liquid and gaseous. Similarly, in considering valency, it is well to remember that the "stationary" state—so to speak—is in this case one in which a certain geometric stability has been reached.

In the whole domain of science involving energy considerations, incompatibilities of these kinds appear. The quantum theory and the ordinary theory of radiation are in conflict at one extreme, while they blend at the other. The theory of relativity negatives certain ideas of Newton which have been thoroughly established for many years. Here, too, at the extreme of great differential speeds, the two theories are in conflict, the Einstein theory giving the correct answer in this case. At the other extreme where slow speeds are involved, either theory will give the correct answer, *i.e.*, the introduction of the relativity theory does not modify the calculations arrived at by the Newtonian method—the classical mechanics. In valency problems the same conflict exists, and in certain cases the answer is the same by either theory, *e.g.*, the ordinary valence theory or that centred round the octet theory, but the latter seems to include the former, that is to say it is not necessary to change theories in passing from one extreme to the other.

One point might be made here, and that is that the reason for this conflict possibly lies in the overlooking of some important factor common to the conflicting theories; and which, if appreciated, would help to clear up matters. First order fractional atomic weights were cleared up by isotopes, although calculations had been made to show how the mass might become "fractioned," as it were, by energy conditions. The discrepancies between Newtonian calculations and observed motions of bodies—electron emissions and the planet

Mercury—have been cleared up by Einstein's theory, which formulates the relative view of necessity involved in the electron case, and similarly in the case of Mercury, but with more elaboration as space physics—so to speak—enters into these problems. The octet theory clears up outstanding difficulties of the older theories.

Now Bohr, in the later developments of his theory, claims that the octet scheme involving the sharing of electrons can be considered in terms of electron orbits so arranged as to unite the atomic nuclei substantially as they are bound according to the static theory. "In fact, the tendency seems towards a Rutherford-Bohr-Lewis-Langmuir atom"—as stated in my *Atomic Theories*, page 137. It is profitable for everyone to become interested in the problems that are engaging the attention of many of the leading scientists of the world.

#### COMPRESSIBILITY, INTERNAL PRESSURE AND ATOMIC MAGNITUDES.

By THEODORE W. RICHARDS,  
Wolcott Gibbs Memorial Laboratory,  
Harvard University.

The object of this paper is primarily to evaluate the respective bulks of the atoms of elements in combination, from the study of the compressibilities of the individual elements and the contraction which occurs during combination. The outcome led also to many other considerations concerning the forces which hold molecules together in the solid and liquid state. The following points in particular are emphasised.

1. Internal pressure is defined for the purpose of the present article as the pressure exerted by the force of affinity, either chemical or cohesive.

2. Bridgman's pressure-volume relations for elements, experimentally determined as far as 12,000 atmospheres, are shown to be represented roughly by hyperbolas of the general type:  $(p+P)(V-B)=K$ .  $P$  and  $K$  increase and  $B$  diminishes with increasing external pressure, but the simple equation just given serves as a sufficient approximation for the present purpose, since with great pressures these contrary changes partly counterbalance one another.  $P$  indicates internal pressure;  $B$  is a function which represents the fact that the atom is less compressible than a perfect gas would be under the same conditions of pressure, volume and temperature. In such

substances as copper, gold, etc., both  $P$  and  $B$  are very large.

3. It is shown that Bridgman's values for the pressure-volume relations of potassium and sodium are very similar, the difference being chiefly due to the fact that sodium possesses a much higher internal pressure than potassium. Therefore it is legitimate to use the sodium values as a continuation of the potassium curve. In this way a curve corresponding approximately to the equation  $(p + 25,800)(v - 0.20) = 20,650$  for the compression of 1.000 cc. of potassium from zero to perhaps 40,000 atmospheres external pressure.

4. From my own values for the compressibility of chlorine, bromine and iodine, and Bridgman's for phosphorus trichloride, similar (although less trustworthy) curves for chlorine and bromine are constructed. These, like the curves of all other polyatomic substances of low boiling-point, are much more flexed than the potassium curve. The reasons for this greater flexure are indicated. The chlorine curve is extrapolated by means of the equation  $(p + 5,300)(v - 0.50) = 2,650$ , which corresponds to the curvature under the highest pressures employed experimentally.

5. The above equations, which give a reasonable picture of the compression of these solids and liquids and are probably capable of moderate extrapolation without great risk, give a new approximate means of estimating internal pressures.

6. From these curves, reduced to a gram-atom basis, taking account of the internal pressures as indicated by the equations in the several combinations, the volumes of these components in combination and the atomic diameters in the salts, as compressed by the mutual affinities, were computed. The atomic diameters thus computed are given in the following table in comparison with earlier values which I computed by an entirely different method, also depending upon the same fundamental idea.

#### ATOMIC DIAMETERS.

	New values.	Earlier values.
Potassium, in chloride .....	3.46	3.5
Potassium in bromide .....	3.56	
Sodium in chloride .....	2.85	2.9
Sodium, in bromide .....	2.92	
Chlorine, with potassium ..	2.82	2.8
Chlorine, with sodium .....	2.78	
Bromine, with potassium ..	3.04	3.1
Bromine, with sodium .....	3.03	

7. The compressibility of the products, calculated from these considerations, corresponds as closely as could be expected with the actual compressibilities of the compounds in question. This fact confirms the results of the extrapolation of the curves. Otherwise, the extrapolation might seem excessive.

8. The outcome furnishes a striking quantitative confirmation of the theory of atomic compressibility, which has been a subject of so many earlier contributions, and supports this theory in every respect, affording important aid in throwing light upon the nature of the atoms. This theory which was first advanced in its present form in 1901, maintains that the chief cause of changing atomic volume is change of internal pressure. In different chemical combinations atoms must be subject to very different pressures from the several mutual affinities which bind them together. Hence their bulk must depend chiefly upon the magnitude of these pressures, and upon the compressibility of the elements concerned. The investigation is being continued, and highly interesting further results have already been obtained.—(*From the Proceedings of the U.S. National Academy of Sciences, 1923, IX., 73.*)

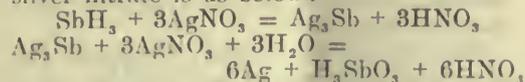
#### THE DETECTION OF TRACES OF STIBINE.

BY EDWARD J. WEEKS, B.Sc., F.C.S.

In some work on the preparation of stibine it was found necessary to devise a method by which slight traces of this substance could be detected quickly without using the mirror test.

The following method was found to show the presence of stibine in a gas, even when it was only present to the extent of 0.05 per cent. by volume.

According to H. Reckleben (*Ber.*, 1909, XLII., 1458-1464) the action of stibine on silver nitrate is as below:



The silver is deposited as a black precipitate.

Hence a glass tube was taken with a diameter of about 5 mm. and about 20 cm. in length. A drop of silver nitrate was inserted in the tube and allowed to run down the sides so as to moisten the inside of the

tube. The experimental gas was then passed through the tube, and a brown stain was produced at once, even when only a trace of stibine was present.

*Sir John Cass Institute.*

April 25, 1923.

#### GENERAL NOTES.

##### THE MINERAL PRODUCTION OF NEW SOUTH WALES.

Mr. A. Simpson, H.M. Trade Commissioner at Sydney, has forwarded to the Dept. of Overseas Trade a statement of the mineral production of New South Wales for 1922.

It is stated that the value of the output of minerals for the year has been ascertained to be £14,274,770, an increase of £266,122 compared with the previous year, mainly owing to renewed activity on the Broken Hill Field.

The aggregate value of all minerals won to the end of 1922 is £350,113,801.

##### *Coal, Coke, and Oil Shale.*

The quantity of coal wrought during the year amounted to 10,183,133 tons, a decrease of 610,254 tons compared with 1921.

The output of oil shale for the year is 23,467 tons, valued at £60,641; a decrease of 9,022 tons and £16,739 in value compared with 1921.

The diminished smelting operations at Newcastle and Lithgow had a very serious effect on the coke manufacturing industry, the production for 1922 being 240,229 tons, valued at £382,926 as against 592,097 tons, valued at £1,029,694 during the previous year.

##### *Gold.*

The aggregate of gold won in the State up to the end of 1922 amounted to 14,873,939 ounces fine, valued at £63,180,442. The production for 1922 showed a further diminution, the yield being 25,222 ounces fine, valued at £107,139. Dredging operations contributed approximately one half of the yield for the year, the principal gold producing mining divisions being Gundagai £18,028. Canbeleg £16,000, Adelong £15,915, Hill End £11,706, and Araluen £3,155.

The yield for 1922 represents less than 1 per cent. of the total value of the mineral production of the year, and this branch of the industry is steadily declining in favour of mining for economic minerals.

*Silver, Lead, and Zinc.*

This branch of the industry is rapidly becoming normal. Many of the Broken Hill Mines were in active operation throughout the year, and production was greatly in excess of 1921. The value accruing to the State from the products of the silver, lead and zinc mines for 1922 amounts to £3,731,566, an increase of £2,120,747 compared with 1921.

The closing down of the Sulphide Corporation Works at Cockle Creek has resulted in a decreased output of silver and lead (pig), and a corresponding increase in the despatches of ore and concentrates for treatment at Port Pirie.

The quantity of ore raised on the Broken Hill Field was 640,064 tons, an increase of 22,731 tons on 1921.

The output from the Yorrandorie field is valued at £64,630, an increase of £14,056.

*Copper.*

The value of the output of copper for 1922 was £36,233, a decrease of £5,034 compared with 1921. Practically all the important mines remained closed during the year, but as the market is showing an upward tendency, an augmented production may be recorded for 1923.

*Tin.*

The value of the tin ores produced in 1922 is £154,698, or a decrease of £8,753 compared with 1921.

Tin mining was restricted on account of low markets and high costs, and in the New England district dredging operations were also retarded by lack of water. If the present price of tin is maintained, the output for 1923 should show a marked advance.

*Ironstone.*

The production of pig iron from the New South Wales ores amounted to 54,856 tons, which represents a considerable decrease. Hoskins Iron and Steel Company, Ltd., at Lithgow, were partly closed during the year. Prospecting operations are being carried on by this company on large areas in the Goulburn, Cuning, Queenbeyan and Tuena Divisions.

In addition, 988 tons of ironstone, valued at £1,274, were raised and used by smelting companies for fluxing purposes.

Of iron oxide, 1,381 tons were raised and used for the manufacture of pigments and by gas companies for purifying purposes.

*Limestone.*

Of Portland cement, 187,800 tons were manufactured during the year from limestone raised in the State representing an in-

crease of £14,466 in value as compared with 1921.

The output for other minerals is as follows:—Alumite £740, arsenic £14,818, asbestos £11,418, bismuth £939, chrome £1,095, clay £13,464, diamonds £1,300, dolomite £800, magnesite £3,231, manganese £7,194, marble £1,900, molybdenite £320, opal (noble) £15,150, platinum £1,182, silica £5,577, sundry minerals £6,942.

Owing to the low prices ruling there was no production of antimony, scheelite, nor wolfram, and only small quantities of bismuth molybdenite were obtained.

Mining for chrome, dolomite, magnesite, manganese, and silica was very seriously affected by the reduced operations carried on by the iron and steel works.

## GERMANY'S POTASH AND NITROGEN INDUSTRIES.

Since April 6<sup>th</sup> the Potash Syndicate has introduced a small price reduction. This is of little avail from the viewpoint of increasing sales. The general opinion is that the reduction of coal prices is too slight to cause reduction in potash prices. It is also thought that a reduction of potash prices would hardly bring about a revival of business, as the agricultural industry, expecting further declines, holds back its orders.

The position of the potash works will soon necessitate short time working. Many works are already on short time, and probably during the next few months will have to work on stock to a greater extent than ever. Accumulation of stock entails heavy expenditure. Proceeds derived from export are no longer so considerable as formerly, and thus do not afford the necessary compensation. The rock salt business, which used to bring in considerable sums to the works, is at a complete standstill. Credit is limited and the complete closing down of works can only be avoided if the necessary working capital is obtained, and nothing remains, therefore, but to have recourse to the open market.

With regard to nitrogen, it appears that since 1913 the German consumption of nitrogen has doubled. During the last financial year, German agriculture required 365,000 tons of nitrogen, *i.e.*, 12.2 kilos for every 2.47 acres. These arrangements for increasing the productivity of German agriculture, which have been reflected in har-

vest results, had only become possible by making German nitrogen requirements more independent of foreign sources. The Haber Bosch process used by the Badische Anilin und Sodafabrik and brought to its highest technical perfection, put an end to the former monopoly of saltpetre.

At the present time the Leunawerk works are still fully employed, but anxiety is felt for the future. Statements to the effect that the demand for sulphate of ammonia has greatly diminished and has even come almost to a standstill have been confirmed.

### FAST DYES.

#### NEW RECORD CLAIMED FOR A LANCASHIRE PROCESS.

A dyeing process discovered in Lancashire laboratories achieved what is claimed to be a record test during the Drapery and Textile Exhibition, recently held at the Agricultural Hall, London.

For a fortnight, cambries, piques, ratines and zephyrs in various pinks, blues, reds, greens, and other shades were boiled in a mixture of strong soap and soda water. Not one, as a result of this strenuous treatment, showed signs of fading.

The test began on the Monday the Exhibition opened, and the materials were boiled continuously. The colours are all made by British dyemakers, and this process leaves them, for the entire life-time of the material, absolutely fast to boiling, bleaching, sunlight and seaside air.

### UNIVERSITY OF LEEDS.

#### CHEMISTRY PROFESSORSHIP.

Dr. R. W. Whytlaw-Gray, O.B.E., Ph.D., Fellow of University College, London, was appointed Professor of Chemistry at the University of Leeds as from October 1 next, in succession to Professor Arthur Smithells, F.R.S. Dr. Whytlaw-Gray was educated at St. Paul's School, London, and at University College, London. From 1900 to 1902 he worked under Sir William Ramsay on a redetermination of the atomic weight of nitrogen. This work was completed in the laboratory of Professor Richard Anschutz in the University of Bonn. On his return from Germany in 1906, Dr. Whytlaw-Gray was appointed on

Sir William Ramsay's staff at University College, London, and in 1908 he became Assistant Professor. While on the staff of University College, Dr. Whytlaw-Gray conducted important investigations on the physical constants of gases, and was associated with Sir William Ramsay in the well-known work on radium emanation (niton). This work involved exceptional experimental difficulties, less than one-tenth of a cubic millimetre of the gas being available. With this almost infinitesimal quantity Messrs. Ramsay and Whytlaw-Gray succeeded in determining its physical properties, thus proving that the emanation belonged to the helium family of elements. In connection with this very delicate work, Dr. Whytlaw-Gray constructed a specially designed balance, which was sensitive to 1/250 thousandth of a milligramme. Since 1914 Dr. Whytlaw-Gray has been science master at Eton College. During the war he also acted as civilian chemical adviser to the Chemical Warfare Committee, and devoted all his spare time to research on the chemical problems involved in gas warfare. This work has been continued and extended since the Armistice, and the results of his investigations have been exceptionally important.

### CERAMIC DEPOSITS OF SASKATCHEWAN.

A considerable amount of interest is being displayed by ceramic experts in the numerous deposits of valuable clays to be found in the Province of Saskatchewan—these ranging from the lower grades used in the manufacture of bricks and tiles to a kaolin which, it is claimed, burns as white, if not whiter, than the British product.

In this connection the Provincial authorities have secured, through the Saskatchewan Bureau of Labour and Industries, the services of a fully-qualified ceramic engineer, in the person of Professor W. G. Worcester, who is engaged in the compilation of data for the perusal of prospective investors. Although the investigations made up to the present are only in their initial stages, the Saskatchewan Bureau of Labour and Industries is desirous of bringing the information already compiled to the attention of British clay-workers, and has, therefore, sent over to the High Commissioner for Canada in London a bulletin on the Clays of Saskatchewan, which it is

thought may interest parties in Great Britain likely to be willing to undertake development work in this field in Western Canada.

The article in question, with accompanying photographs, may be consulted at the office of the High Commissioner for Canada, 19, Victoria Street, London, S.W.1.

#### DRUGS REQUIRED IN SWITZERLAND.

H.M. Consul-General at Zurich (Mr. Ernest G. B. Maxse, C.M.G.), reports that a firm of wholesale and retail druggists in Schaffhausen, is desirous of purchasing pharmaceutical and druggists' specialities; or preferably of securing the representation for Switzerland of British manufacturers of such goods.

Application for further particulars regarding this enquiry should be addressed to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1, quoting reference 19094/FW/CC.

#### PHOTOGRAPHIC MATERIALS FOR ECUADOR.

His Majesty's Consul-General at Quito (Mr. R. C. Michell) has transmitted a report on the market for photographic materials in Ecuador, a copy of which may be obtained by British firms upon application to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1. (Ref. No. 905/2/F.G./C.C.)

#### F.B.I. AND RAILWAY RATES.

The question of railway rates came before the Grand Council of the Federation of British Industries on April 18, when Sir Eric Geddes presided.

The following resolution was passed:—

"That the President be authorised, acting in consultation with the Transport Committee, to lodge an application with the Railway Rates Tribunal for a general reduction of rates, to take effect on August 1, if, at any time, he should consider that the situation demands such action."

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL SOCIETY.

Papers read at the meeting on Thursday, April 26:—

W. A. BONE, F.R.S., D. M. HEWITT, and D. T. A. TOWNEND.—*Gaseous Combustion at High Pressures. Part III.: The Energy-absorbing Function and Activation of Nitrogen in the Combustion of Carbon Monoxide.*

It is shown that nitrogen can no longer be regarded as an inert gas in the combustion of carbon monoxide, because when present as a diluent in a mixture of  $2\text{CO} + \text{O}_2$  undergoing combustion in a closed vessel under high pressure it exerts a peculiar energy-absorbing influence upon the system, far beyond that of other diatomic diluents (e.g., excess of  $\text{O}_2$  or  $\text{CO}$ ) or even of argon. This influence (a) retards attainment of maximum pressure, and (b) diminishes maximum temperature attained in explosion, in a much greater degree than can be accounted for on the supposition of its acting merely as a diatomic diluent.

The energy so absorbed by nitrogen during the combustion period is slowly liberated as the system cools down after attainment of maximum temperature, and consequently the rate of cooling is greatly retarded for a considerable time. These effects are very marked in the case of a carbon monoxide-air mixture ( $2\text{CO} + \text{O}_2 + 4\text{N}_2$ ), and much more so in that of a mixture ( $2\text{CO} + \text{O}_2 + 6\text{N}_2$ ), undergoing combustion under high pressures. In consequence of such energy-absorption, nitrogen becomes chemically "activated" in such explosions, remaining so for a considerable time after attainment of maximum pressure, while slowly reverting to its normal condition. Whilst in this "activated" condition it will combine with oxygen, forming oxides of nitrogen.

If no nitrogen be present in the mixture exploded (e.g., in an undiluted mixture  $2\text{CO} + \text{O}_2$ ), carbon monoxide burns in oxygen at high pressures almost (but not quite) as rapidly as does hydrogen. Indeed, it would appear as though the usually considered "slow-burning" character of carbon monoxide as compared with hydrogen is not so much inherent in the gas itself as it is conditioned by the presence of nitrogen in the burning mixture.

There is no correspondingly large (if any) energy-absorbing effect (other than purely "diluent") when nitrogen is present in hydrogen and oxygen mixtures similarly undergoing combustion, and there is no evidence of nitrogen being then activated. Indeed, the presence of even a small percentage (two or three) of hydrogen in a carbon monoxide-air mixture undergoing combustion is sufficient to prevent any material activation of the nitrogen. It would thus seem as though the peculiar influence of nitrogen in  $2\text{CO} + \text{O}_2$  explosions is due to its ability to absorb the particular quality of radiation emitted when CO and :O (but not when CO and :OH<sub>2</sub>) react; such radiation is known to be of a different wavelength from that emitted during the flame-combustion of hydrogen. In other words, there seems to be some constitutional correspondence between CO and N<sub>2</sub> molecules, whereby the vibrational energy (radiation) emitted when the one reacts with :O is of a quality readily absorbed by the other, the two acting in resonance.

R. A. WATSON WATT and E. V. APPLETON, D.Sc.—*On the Nature of Atmosphericics*. Communicated by Sir Henry Jackson, F.R.S.

The paper describes observations with a cathode ray oscillograph, on the temporal variations of the electric force occurring in radio telegraphic atmosphericics. It is shown that approximately faithful reproduction of the field changes can be assured by using a highly damped antenna whose time constant is kept much less than the duration of the atmosphericic.

The principal constants of six hundred typical atmosphericics, of which five hundred were delineated by an "eye and hand" method, are examined. A bare majority are quasi-periodic, consisting normally of one complete oscillation, of duration 2,000 micro seconds, the mean change of field being 0.128 volts per metre, with no marked unbalanced transport of electricity on the whole group.

A second group of almost equally frequent occurrence consists of aperiodic impulses, of duration generally about 1,250 micro seconds, but frequently reaching 0.025 of a second, the mean change of field being 0.125 volts per metre, with a seven to one numerical predominance of discharges tending to carry negative electricity to earth in the receiving antenna.

The form of the aperiodic type of atmos-

pheric is shown to include a period of growth to maximum field strength whose duration is little short of the decay period.

I. MASSON, D.Sc., and L. G. F. DOLLEY.—*The Pressures of Gaseous Mixtures*. Communicated by Prof. F. G. Donnan, F.R.S.

Measurements have been made at 25° of the compressibilities up to 125 Atm. of ethylene, argon, oxygen, and a series of binary mixtures of these.

The volume of a compressed mixture usually exceeds the sum of the separate volumes of its two components, the excess depending on the molecular ratio of the two gases chosen and upon the pressure. Thus with an equimolecular mixture of argon and ethylene at 80 Atm. the volume is greater than the additive value by 24 per cent. At a given pressure there is an "optimum" composition, and with a given composition there is an optimum pressure. Oxygen-ethylene mixtures behave quantitatively in the same way as argon-ethylene; oxygen and argon when mixed show a negligible volume increase, and are individually equally compressible.

It is further shown that the pressure of a mixture at high densities exceeds the sum of those measured for the separate constituents; at moderate densities it is definitely less. The former occurrence is due to the actual space filled by the molecules; the latter is due to a mutual cohesion between each. The significance of this was discussed.

Papers read in title only:—

T. R. MERTON, F.R.S., and R. C. JOHNSON.—*On Spectra associated with Carbon*.

The spectral changes due to the admixture of helium to vacuum tubes containing carbon compounds, and the conditions for isolating the band spectra associated with carbon have been investigated. In particular the "high pressure CO" bands can be isolated almost completely under appropriate conditions. The "comet-tail" bands are found in vacuum tubes containing helium and carbon monoxide under appropriate conditions.

In the presence of helium the distribution of intensity in the comet-tail bands differs markedly from that observed by Fowler in tubes containing carbon monoxide at very low pressures, and the wave-lengths of the heads of the bands have been re-measured. By the admixture of hydrogen

the comet-tail bands are replaced by a system of triplet bands which have not been isolated hitherto, and the wave-lengths of the heads of these bands have been measured and found to fall into two distinct band series.

In helium containing a small quantity of carbon monoxide a new line-spectrum has been observed under suitable conditions of excitation, and it is believed that this spectrum is to be attributed to carbon.

W. R. BOUSFIELD, F.R.S., and C. ELS-PETH BOUSFIELD.—*Vapour Pressure and Density of Sodium Chloride Solutions.*

The purpose of the author's was to obtain a standard set of V.P. determinations at 18° C. for aqueous solutions of NaCl at all concentrations. The method employed was to introduce water and the solution into the legs of a V tube surmounting a barometric column of mercury. Special precautions were taken to exclude air. This necessitated the boiling of the solutions so that they became of unknown concentration. The V.P. observations were therefore primarily correlated to the densities of the solutions. To correlate with the concentrations, a complete set of density observations at 18° C. were made on solutions of known concentration accurate to + 2 in the fifth place of decimals.

Incidentally a method of determining molecular weights by combined observations of the density and V.P. of dilute solutions is given.

F. A. LINDEMANN, F.R.S., and G. M. B. DOBSON.—*A Note on the Temperature of the Air at Great Heights.*

The relatively high pressure of the atmosphere above 60 km., which was discussed in a previous paper, would appear to be due to absorption of an appreciable amount of direct solar radiation. Thus there should be a large variation in temperature at these great heights. Various ways in which such a variation might be shown are considered and some evidence of its existence is found.

G. H. HARDY, F.R.S., and J. E. LITTLEWOOD, F.R.S.—*On Lindelöf's Hypothesis concerning the Riemann Zeta-function.*

The paper contains a number of necessary and sufficient conditions for the truth of the hypothesis, some stated in terms of the Zeta-function itself, and others in terms of the arithmetical functions which

occur in the "lattice-point problems" of Dirichlet and Piltz.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

The Friday evening discourse on May 4, at 9 o'clock, will be delivered by FREDERICK SODDY, F.R.S. The subject is *The Origins of the Conception of Isotopes.*

On Tuesday, May 1, SIR ARTHUR KEITH, M.D., LL.D., F.R.S., Sec. R.I., Fullerian Prof. of Physiology, gave a lecture on *The Machinery of Human Evolution: (IV.) Are our Bodies Changing?*

On Thursday, May 3, PROF. J. T. MAC-GREGOR-MORRIS, M.I.E.E., M.R.I., gave a lecture on *Modern Electric Lamps: (II.) Glowing Solids in Gases.*

On Saturday, May 5, LEONARD WILLIAMS, M.D., M.R.I., will give a lecture on *The Physical and Physiological Foundations of Character.* (Lecture II.).

#### ROYAL SOCIETY OF ARTS.

On Monday, April 30, the Howard Lecture on *The Development of the Steam Turbine*, was delivered by STANLEY S. COOK, B.A. (CANTAB.), M.I.N.A., M.I.M. (Parsons Marine Steam Turbine Co.).

#### THE CHEMICAL SOCIETY.

At the Ordinary Scientific Meeting, held on Thursday, May 3, the following papers were read:—

*Change of Properties of Substances on Drying.* Part II. H. S. BAKER.

*The Sodium Salts of Phenolphthalein.* H. BASSETT and P. HALTON.

*The Action of Thio-sulphates on Cupric Salts.* H. BASSETT and R. G. DURRANT.

*The Conditions of Reaction of Hydrogen with Sulphur.* Part II.: *The Catalytic Effect of Oxygen.* Part III.: *On the mechanism of the Reaction of Hydrogen with Sulphur and its Catalysis by Oxygen.* R. G. W. NORRISH and E. K. RIDEAL.

*Studies of Electrovalency.* Part II.: *Co-ordinated Hydrogen.* T. M. LOWRY.

*Investigations on the Dependence of Rotatory Power on Chemical Constitution.* Part XX.: *The Rational Study of Optical Properties.* H. HUNTER.



#### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

A meeting of the Society was held on Wednesday, May 2, when the following papers were read:—

*The Quantitative Determination of Hemp and Wood in Papers containing these two Fibres*, by WILLIAM DICKSON, F.I.C.

*The Estimation of Fat, Lactose and Moisture in Dried Milks*, by H. JEPHCOCK, M.Sc., F.I.C.

*The Estimation of Lactose by the Polarimetric and Gravimetric Methods*, by A. L. BACHARACH, B.A., A.I.C.

*The Melting Point and Iodine Value of Refined Natural D. Camphor*, by MAURICE S. SALAMON, B.Sc.

*The Presence of Barium and Strontium in Natural Brines*, by A. G. FRANCIS, B.Sc., F.I.C.

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#### THE INSTITUTION OF ELECTRICAL ENGINEERS.

At a meeting of the Wireless Section, in the Lecture Theatre of the Institution, on Wednesday, May 2, PROFESSOR C. L. FORRESCUE delivered a lecture entitled *The Design of Inductances for High-Frequency Circuits*.

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#### SOCIETY OF GLASS TECHNOLOGY.

The sixth annual general meeting of the Society of Glass Technology was held in Sheffield, on Wednesday, April 18, the President, Prof. W. E. S. Turner, D.Sc., in the chair. The formal business included the election of the following officers to fill vacancies arising according to the "Constitution and Rules" of the Society:—

*President*: Prof. W. E. S. Turner, D.Sc. (re-elected).

*Vice-Presidents*: E. A. Coad-Pryor, B.A., W. J. Gardner.

*Members of Council*: F. F. S. Bryson, M.A., B.Sc., F.Inst.P., Violet Dimpleby, B.Sc., Major G. V. Evers, Col. S. C. Halse, T. Teisen, B.Sc., C.E.

*Treasurer*: Joseph Connolly (General), Wm. M. Clark, Ph.B. (American).

*Hon. Secretary*: S. English, M.Sc.

*Auditors*: Edward Meigh, M.Sc., Dennis Wood, F.S.A.A.

The President's address on *The Year in Review in the World of Glassmaking*, was

taken as read, the main business of the meeting being a general discussion on *Works Organisation*. Mr. W. W. Warren (Messrs. Lemington Glassworks, Ltd.) opened the discussion with a paper entitled *Organising for Production from Pot Furnaces*. After a discussion on this paper (which had already been presented at the Newcastle meeting in February), the case for "Tank-furnace works organisation" was presented by Mr. T. C. Moorshead (Messrs. United Glass Bottle Manufacturers, Ltd.), who said that organisation as applied to a manufacturing industry might be defined as a combination of men arranged or distributed in parts or groups with proper officials, managers, and foremen, and so co-ordinated that they were able with the aid of such machines and tools as they might have available, to produce a finished article efficiently. If they could not say assuredly that each of their groups was composed of capable men, each group in charge of a capable foreman, the foremen all capable, and co-operating under a capable superintendent or shift manager, or whatever they might call him; who was responsible? He believed that the man really responsible for the losses in plant efficiency was the active head of the institution. He endorsed the opinion of industrial engineers and efficiency experts who stated that the average manufacturing plant had only 50 per cent. efficiency, and that also 80 per cent. of this tremendous loss of efficiency was due to the manager, or to a lack of proper or efficient management. The difficulties which beset the factory manager every day might all be traced back to inefficiency on the part of the management, and probably to three things:—(1) Lack of foresight; (2) lack of thorough knowledge of the factory operations; (3) lack of initiative. The causes for these losses could be grouped under five headings:—(1) Faulty raw material; (2) poor labour, that is, incapable, indifferent and disloyal employees; (3) poor attendance; (4) large labour turnover, or ratio of men leaving to the number of men on the payroll; (5) machine or mechanical breakdowns.

1.—*Faulty Raw Material*: It was urged that the buyer, or preferably a works chemist, should investigate the sources of supply to make provision for constant and regular supplies, keep a sufficient quantity in store at all times to ensure the factory against shut downs in case of failure of de-

liveries, to analyse frequently the materials for purity, and to see that they came up to specifications.

2.—*Poor Labour* was a difficult problem and should be dealt with at the source.

3.—*Poor Attendance* was a fundamental principle in dealing with their difficult problems to make a man's work interesting. This might be done first of all by being sure that employees understood what they were doing and why. The more they knew about the material they worked with, the better. Weekly managers' and foremen's meetings are held, full and complete records or minutes of which are kept and copies circulated to those who were present. One copy is also sent to the head office.

4.—*Large Labour Turnover*: To prevent the wastage due to this, work should be made agreeable. It was also necessary to regularise it. Every man should be given identity. A great many manufacturing plants were going so far as to make a careful analysis of each piece of work.

5.—*Machine or Mechanical Breakdowns* were the least wearisome cause of efficiency loss. In nine cases out of ten, machine breakdowns were due to lack of foresight; failure on the part of the man responsible for either the operation or upkeep of the particular machine to anticipate troubles; failure to see that spares for vital parts of the various machines were in store, and failure to keep all moving parts properly oiled and the machines clean, all of which brought us back to the human element and organisation.

Mr. Moorshead concluded his paper by emphasising the responsibility that rests on the foremen, and suggested the questions a manager might ask himself in selecting his foreman or determining his capabilities.

Col. S. C. Halse (Messrs. J. Lumb & Co., Ltd.) said that at his works, after installing a set of new machines, they had daily conferences, including everyone really concerned in the output of their machines. By analysing the figures obtained from day to day they had increased production, and were able to trace nearly every bottle dropped on to the conveyer.

#### THE INSTITUTE OF METALS.

DR. W. ROSENHAIN, F.R.S., delivered the thirteenth annual May lecture before the Institute of Metals on Wednesday, May 2. His subject was *The Inner Structure of*

*Alloys*, upon which much debated matter a flood of light was thrown.

#### MANCHESTER MEETING.

A further meeting of the Institute (the annual autumn gathering) will be held in Manchester on September 10-13. A ballot for the election of Members and Students desirous of participating in this and other meetings will take place on July 12th, the necessary membership particulars being also obtainable from the Secretary, Mr. Shaw Scott, The Institute of Metals, 36-38, Victoria Street, S.W.1.

#### PHYSICAL SOCIETY OF LONDON.

At the meeting held on Friday, April 27, the following papers were read:—

*The Analysis of Bubbles in Glass*, by the RESEARCH STAFF of the General Electric Company, London.

*A Simple Regenerative Vacuum Device and Some of its Applications*, by H. P. WARAN, PH.D.

*Application of the Eötvös Torsion Balance to the Investigation of Local Gravitational Fields*, by CAPT. H. SHAW and E. LANCASTER-JONES, B.Sc.

Demonstrations were given as follows:

*An Electromagnetic Inductor*, by L. F. RICHARDSON, F.INST.P.

*An Experiment Demonstrating Time-Lag in Vision*, by DR. F. LL. HOPWOOD.

At the meeting held on March 23, Alexander Russell, M.A., D.Sc., in the chair, papers on *A New Moving-Coil Galvanometer of Rapid Indication* and *A Thermopile for Measuring Radiation*, by DR. W. J. H. MOLL, University of Utrecht, were read by Mr. R. S. Whipple in the author's absence.

The galvanometer is designed to secure rapid indication and steadiness of reading without unduly sacrificing sensibility. The coil is long and narrow, and therefore of small moment of inertia: the mirror is supported by the wires forming the coil, between which it is slipped, and the coil is supported between an upper and a lower vertical wire, as distinct from strips, made of silicium bronze and put in tension.

The thermopile is designed to be quick-reading and free from zero-errors, as well

as sensitive. The cold junctions are in contact with metal masses which keep down their temperature, and in order that the hot junctions may have small heat capacity the bi-metallic strips composing the thermopile are made of plates of constantan and manganin silver-soldered along an edge, rolled in a direction parallel to the edge into thin foil, and then cut into strips perpendicular to the edge.

#### Discussion.

Mr. F. E. Smith commented on the strikingly dead-beat character of the indications given by both instruments. He suggested that the thermopile strips might be reduced to even a less thickness than 0.005 mm. by solution in acid. The galvanometer seemed to have been designed to produce what, with a single fibre suspension, would have been an extremely sensitive instrument, but then the supporting wires were put in tension to reduce the period. Would it still be possible in these circumstances to obtain the required sensibility?

Dr. R. T. Beatty recalled the time when it was necessary to work with a bismuth-iron couple of great heat-capacity and an insensitive Thomson galvanometer. Later came the Paschen astatic galvanometer, but this instrument required such heavy protection from stray magnetic fields that few cared to use it. Dr. Moll's improvements should make possible an advance in measurements of the distribution of energy in the spectrum, e.g., in the H and He spectra.

Mr. C. R. Darling suggested that the apparatus might be applied to measure the distribution of energy in the spectrum of a glow lamp.

Mr. J. Guild inquired if the present galvanometer differs materially from that exhibited by Dr. Moll three years ago, and what is the number of junctions per cm. in the linear form of the thermopile. If silicium bronze is similar in its properties to phosphor bronze the tension of the supporting wires of the galvanometer would have a serious effect on the sensibility of the instrument.

Mr. L. F. Richardson said that he thought Dr. Moll's thermopile admirable for indoor use. For work out of doors, where a rock salt cover could not be used and gusts of wind could not be excluded, Mr. W. H. Dines had found it desirable to make the hot and cold junctions of as nearly the

same thermal capacity as possible, so that air currents might affect both equally.

Mr. R. S. Whipple, in reply, said that the difficulty of rolling the strips is immense, and Mr. Smith's suggestion as to solution in acid was well worth trying, though there might be difficulties due to unequal chemical action. He agreed that, although there is no instrument as sensitive as the Paschen galvanometer, this is troublesome to use.

#### *A Note on Aberration and the Döppler Effect as Treated in the Theory of Relativity*, by CAPT. C. W. HUME, M.C., B.Sc.

In older text-books aberration is explained as due to the compounding of the velocity of light with the velocity of the earth relative to the ether; hence at first sight the phenomenon appears to conflict with the principle of relativity. The paper gives simple methods of treating this problem consistently with the Restricted Principle, and of finding the Döppler effect. In each case the result differs from the non-relativity result by terms of the second and higher orders in  $v/c$ .

#### A demonstration was shown by Mr. C. R. DARLING and HON C. W. STOPFORD, entitled *Experiments on the Production of Electromotive Forces by Heating Junctions of Single Metals*.

When a circuit is closed through a junction of a cold metal with a hot piece of the same metal, large E.M.F.'s are often noticed. As example a bare copper wire was connected to the terminals of a galvanometer. The wire was cut at the middle, one of the cut ends heated and brought into contact with the cold end, when a large deflection was obtained. Electromotive forces up to 0.25 volt may thus be produced.

#### Discussion.

Mr. J. S. G. Thomas called attention to an account of experiments somewhat similar given by Prof. Carl Benedicks in 1920.

Dr. H. Borns said he hardly understood why Mr. Darling was surprised at his strong thermo-electric forces. When he broke his copper wire with a pair of pincers the two ends of the wire would not be strained equally. The one end of his iron rod (and of his graphite rod) was grooved, the other filed to chisel shape. The one end was heated in a gas flame to about 700° C.;

the temperature gradients were very steep, and the conditions were favourable to oxidation and other chemical effects, expulsion of gases (from the graphite), and to pronounced heterogeneity.

Mr. F. E. Smith commented on the extreme difficulty of treating metals in any way without affecting their constitution. In trying to make a junction with E.M.F. as low as  $10^{-7}$  volts he had found it impossible even to cut silver and platinum wires without straining them, and by twisting the wires he obtained a much greater effect. One inference from the omnipresence of thermo-electric voltages is that in the Wheatstone Bridge the galvanometer key ought to be closed before the battery key, contrary to the usual practice.

Dr. D. Owen said that the voltages obtained appeared to be of the order to be expected from thermo-electric currents at contacts of oxides or sulphides of the metals. Had the authors tried the effect with platinum?

Dr. J. A. Harker said that in using the Callendar-Griffiths Bridge some years ago to measure the resistance of copper wire, he had found that if the wire were asymmetrically heated two different values of its resistance were obtained for the two directions of the current through the bridge. The two values drifted further apart with lapse of time. Lord Kelvin regarded the phenomenon as a modified form of the Kelvin effect.

Mr. R. S. Whipple asked whether the E.M.F. obtained is affected by the pressure at the junction. If the effect is chemical, the compression would affect the thickness of any film formed.

Dr. E. H. Rayner said that thermo-electric currents were formerly dealt with very briefly in the text-books. He would like to know how the subject is now handled in the class-room.

Dr. F. Ll. Hopwood said that information bearing on the subject of the demonstration could be found in the published writings of Richardson and Benedicks.

A demonstration of *The Double Refraction due to Motion of a Vanadium Pentoxide Sol, and Some Applications*, was given by Mr. R. H. HUMPHRY, M.Sc.

The effect was first noticed in 1915 by Freundlich, Dieselhorst and Leonhardt. In linear flow the liquid behaves in the same way as a plate of uniaxial crystal cut paral-

lel to the axis and placed with axis parallel to the direction of flow.

The field between crossed nicols was shown to light up near an obstacle interposed in a stream of the liquid. Similar effects due to efflux of the sol from a jet, to the convective stream from an electrically-heated wire, etc., were also shown.

#### Discussion.

Mr. E. Hatschek said that the experiments called for exceptional cleanliness as the sol is very sensitive to electrolytes. Aniline blue is interesting in that it gives colour effects; it has a well-marked absorption band, and behaves like a positive crystal to wave-lengths on one side of the band, but like a negative crystal to wave-lengths on the other side.

Mr. R. W. Paul asked whether the effect of subjecting the liquid to an electrostatic field had been tried.

Mr. J. Guild said he was not satisfied as to the cause of the double refraction. The colloidal particles are too large to have the effect of molecules, and too small to be regarded as transmitting light after the manner of glass dust. In his reading of ultra-microscopic literature he had come across nothing which suggested a satisfactory explanation. In interpreting the appearances obtained by Prof. Coker's method the greatest caution is necessary. The intensity of the effect of a strain or a streamline depends on its direction, and for certain directions-it is impossible to detect a strain at all.

In reply to the discussion Mr. Humphry said that the experiments which were shown were only to be regarded as preliminary, and no interpretation of the observed effects had yet been attempted. It seemed possible by use of this effect to throw more light on stream line problems; and with better apparatus, designed to overcome any tendency towards gelation, useful results might be obtained. The effect of an electric field on the arrangement of the particles had been worked out by Freundlich (*Kapillar Chemie*, 1922), who also explained the production of the double refraction. It is true that with stationary nicol prisms certain stream lines are accentuated, while others may not appear at all; but this difficulty would be overcome by having rotating nicols. The more delicate means of examining polarised light might show effects which were missed with nicol prisms.

## PHYSICS IN INDUSTRY.

The fourth of the series of lectures on this subject, which are being delivered under the auspices of the Institute of Physics, will be given by DR. J. W. MELLOR, of Stoke-on-Trent, and will deal with *The Application of Physics to the Ceramic Industries*.

Sir J. J. Thomson will preside at the lecture, which will be delivered in the hall of the Institution of Electrical Engineers, Victoria Embankment, W.C.2, on Wednesday, May 9, at 5.30 p.m.

A ticket of admission will not be required.

## THE INSTITUTION OF ELECTRICAL ENGINEERS.

*The Design of Inductances for High-Frequency Circuits*, by PROFESSOR C. L. PORTESCUE, Member.

This paper consists of an investigation of the proportions and the arrangement of the winding of high-frequency inductances in order to obtain the minimum ratio of R/L. Both stranded and solid wire coils are dealt with, and the unavoidable limitations arising from the space-factor are considered. Results and tables are given which enable simple comparisons to be made between stranded and solid wire coils having either single- or multiple-layer windings.

## CORRESPONDENCE.

## CAUTION TO INVENTORS.

To the Editor of THE CHEMICAL NEWS.

SIR,—In case the matter may not have been brought to your notice already, I should like to draw your readers' attention to the *Caution to Inventors*, which has been inserted by the Comptroller-General of Patents in the Illustrated Official Journal at the request of the Chartered Institute of Patent Agents:—

"Inventors are advised to beware of suggestions such as are now being issued from a German source to the effect that, for reasons obscurely stated by the German writer, the British inventor should cooperate with him, and in particular should send him by registered letter a sum of

money. The communication is fraudulent, and on no account should money be sent."

I am,

Yours faithfully,

RICHARD B. PILCHER,

Registrar and Secretary.

The Institute of Chemistry,

30, Russell Sq., London, W.C.1.

April 18, 1923.

## ARABIAN ALCHEMY AND CHEMISTRY.

To the Editor of THE CHEMICAL NEWS.

SIR,—Perhaps you will be good enough to allow me to answer the letters of Mr. Whale (March 9), and Mr. Redgrove (April 6), on the question of Geber. I would first make it quite clear that the sole conclusive proof of the identity of Geber with Jabir ibn Hayyan, the famous and historical Muhammedan chemist of the 8th century, would be the discovery of Arabic originals of the Latin works; up to the present this discovery has not been made. I have briefly outlined my position in an article in *Nature* (Feb. 10, 1923), to which, and to the valuable letter of Prof. J. R. Partington in the following number of the same journal, perhaps Mr. Whale and Mr. Redgrove will refer.

There are, however, one or two additional facts which may be of interest: (1) *Geber* is an accurate transliteration of the Arabic *Jabir*, especially as in Egypt and many other parts of the Muhammadan world the letter *j* (*j i m*) is sounded as hard *g*; (2) according to Darmstadtter, *Die Alchemie des Geber*, Berlin, 1922, p. 134, Vincent de Beauvais in cap. 82 of his *Speculum Naturale*, Nürnberg, 1485, refers to Geber as *Jeber*; (3) in mediæval Latin chemical works Geber is often called Geber ebor Haen, which is undoubtedly a transliteration of the Arabic Jabir ibn Hayyan; (4) Boerhaave (1668-1738), professor of chemistry at Leyden University, says in his *Elementa Chemiæ* (Shaw's English translation, 3rd edition, 1753, vol. I., p. 26, footnote, that Golius (1596-1667), professor of mathematics and Arabic at the same University, presented Arabic MSS. of Geber to the Leyden public library, and translated them into Latin; the translation was, he says, published at first in folio and afterwards in quarto, under the title of *Lapis Philosophorum*. From Boerhaave's description of this translation (*loc. cit.*) it is

clear that the work, if not actually the *Summa*, at least bears the closest similarity to it. But the *Summa* and other Latin works were already well known, and had been studied for some three hundred years. Why, therefore, should Golius go to the trouble of translating them from the Arabic unless to provide a more accurate text? It seems to me that the importance of this observation of Boerhaave's is very great. At the same University as Golius, and practically contemporary with him, his information must almost certainly be reliable; he knew the *Summa* and other Latin works and the presumption that Golius' translation is of Arabic originals of these seems overwhelming. If it were otherwise, surely Boerhaave would have mentioned the fact. It is tantalising to find that the Leyden library, if Boerhaave is correct, must have lost these manuscripts, as there are now in it none which can be regarded as originals of the Latin works. However, fresh discoveries of Arabic MSS. are continually being made, and one may hope that other copies of the works translated by Golius may be forthcoming in the future.

(5) The names of many works attributed to Geber correspond with titles of works of the Arabic Jabir ibn Hayyan, as given in the *Kitab at Fihrist* and elsewhere; example (a) *De claritate alchemiæ* with *The Book of Spendour*, (b) *Testamentum Geber* with *The Testament of Jabir*, (c) *The Summa* with the *Compendium*. Unfortunately Arabic texts of these are not yet known.

On the desirability of making translations of all the extant Arabic writings of Jabir ibn Hayyan, I am in entire agreement with Mr. Redgrove and Mr. Whale. I feel, however, that translations without texts are always unsatisfactory, but since publishers are very reluctant to undertake the expensive business of having Arabic type set up, there seems to be no alternative. I have in hand a translation of the *Book of Properties*, from the British Museum MS., and hope to publish a great part of it in a forthcoming book on *Chemical Theory and Practice in Islam*, which I am preparing for the Trustees of the Gibb Oriental Translation Fund.—I am, Sir,

Yours, etc.,

E. J. HOLMYARD.

Clifton College.

April 19, 1923.

#### LABORATORY ENQUIRY.

To the Editor of THE CHEMICAL NEWS.

SIR, — Could any of your readers supply me with the address of a laboratory that would make up a sample from a formula?  
I am, Yours, &c.,

NORMAN URWIN.

3, Percy Avenue, Catchgate, Durham.  
April 19, 1923.

#### NOTICES OF BOOKS.

*Wavelength Tables for Spectrum Analysis*, by F. TWYMAN, F. INST. P. Pp. VIII. + 106. London: Messrs. Adam Hilger, Ltd., 75a, Camden Road, N.W.1. 1923. Price 7s. 6d. net.

This comprehensive treatise is not, as the title conveys, a monotonous page-sequence of tables, difficult of reference and with jumbled data. Instead, it is a first-class text-book of interesting matter, of inestimable value to the analyst.

Referring to the author's preface, it comprises standard wavelengths from 2375 to 8495 I.A., the persistent and sensitive lines of most of the elements arranged under the name of each element, and the most persistent and sensitive lines rearranged in order of wavelengths. The last chapter deals with wavelengths useful in the determination of stellar radial velocities.

In his explanatory matter, the author has rightly paid much attention to the results of Hartley, Pollok, Leonard, and A. de Gramont, briefly showing records of their respective works, and carefully tabulating their data. In a short appendix, the condensed spark produced by means of the Hemsalech coil (quoted frequently by the authorities mentioned above) is described collectively with the requisite observations.

The value of this book is not to be estimated, and we recommend it highly to the notice of our readers. It should run to many editions.

*The Phase Rule and Its Applications*, by ALEXANDER FINDLAY, M.A., PH.D., D.Sc., F.I.C. Fifth edition. Pp. XVI. + 298. London: Longmans, Green & Co., Ltd., 39, Paternoster Row, E.C.4. 1923. Price 10s. 6d. net.

In the course of the rapid development of the various sections of Physical Chemis-

try, in recent years, increasing attention has been paid by investigators to the study of heterogenous equilibria. This has necessitated a very complete revision of some of the chapters of Professor Findlay's classical text-book on the Phase Rule, which we are pleased to note is now in its fifth edition.

Certain sections have been re-written, and much new matter (including 24 fresh diagrams) has been incorporated. The graphical methods, especially those initiated by Jänecke, of representing multi-component systems, have been widely used. They are fully explained for the benefit of students and others not familiar with this mode of expressing results.

Doubtless the present revised edition of this volume in the important series of text-books on Physical Chemistry, edited by Sir William Ramsay and Prof. F. G. Donnan, will be as widely and assiduously studied as its predecessors.

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*The Destructive Distillation of Wood*, by H. M. BUNBURY, M.Sc. (Bris.), B.Sc. (Lond.). Pp. XIX. + 320. London: Benn Brothers, 8, Bouverie St., E.C. 1923. Price 35s. net.

Whilst the destructive distillation of coal has been the subject of numerous treatises, very little attention has been paid to the thermal decomposition of wood. This is somewhat surprising in view of the fact that the distillation of wood comes next in importance to that of coal.

Mr. Bunbury's book is therefore very welcome. In it he has given a good description of the plant and processes used in the distillation of various types of wood. This is followed by a survey of the products of these thermal decompositions and the conditions influencing their respective quantities and composition.

The treatment of the technical aspects of the subject has been well done, and whilst modern processes are adequately described, obsolete methods receive historical mention only.

In the immediate future such processes as the thermal decomposition of wood will receive much more attention than they have hitherto commanded, especially when it is realised that waste wood can be successfully treated.

The information contained in Mr. Bunbury's book will be found of value to in-

dustrial chemists and others interested in this subject. It is a contribution to the chemistry and technology of distillation which deserves, and will doubtless obtain, a place in all scientific and technical libraries.

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#### PUBLICATIONS RECEIVED.

*Nitrate Facts and Figures*, 1923, compiled by A. F. BRODIE JAMES, F.S.S. London: F. C. Mathiesons & Sons, 16, Cophall Ave., E.C. 5s. net.

This is the twentieth year of issue of these statistics, which tend to show that the period of depression in the nitrate industry has passed. The near future seems very hopeful.

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*Mysore Agricultural Calendar*, 1923. Price 1 anna.

This publication contains much useful information for those interested in its 54 pages. That agricultural problems are of a scientific nature is clearly indicated by a perusal of the various methods outlined to combat pests.

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*The Official Handbook*, issued by THE BRITISH ASSOCIATION OF TRADE AND TECHNICAL JOURNALS, LTD. London: Silician House, Southampton Row, W.C.1. Pp. 102. 1923. 1s. net., is full of most interesting data concerning the advertising facilities offered by technical journals.

The restoration of trade rests, to some extent, with the creation of a revitalised market-interest. Prior to the war, British chemicals were in a general state of prosperity, but a damaging cautiousness is extant among purchasers now. To overcome such an attitude, manufacturers must make judicious use of industrial publications, and this is the object of the publishers of the *Handbook*: to advise and keep advertisers in their campaigns—large or small.

Much important information bearing upon these points is enclosed in the prefaces. The book is, in fact, a complete and concise means of reference for all firms who are planning publicity schemes in 1923.

W. Heffer & Sons, Ltd., Publishers, Cambridge, have in the press a volume entitled *The Expert Witness*, by C. AINSWORTH MITCHELL, M.A. (Oxon.), Editor of *The Analyst*.

This book is written on similar lines to and is in many respects a sequel to the author's "Science and the Criminal," which is now in its second large edition. It gives an outline of the latest applications of scientific research to the investigation of criminal problems, and also an account in non-technical language of the use of expert evidence of all kinds, illustrated by reference to old and modern trials.

The nine chapters deal with the latest methods of identification by means of patterns on the feet; by the pores of the skin; by the detection of latent prints on paper, etc.

The latest scientific methods of handwriting are also described, and an outline is given of the author's methods of estimating the age of ink in writing. In the description of Secret Writing there is an account of the scientific evidence given at the trials of German spies.

The last chapter deals with expert evidence in art and with the application of such scientific methods as the use of X-rays to identify old masters.

Messrs. Baillière, Tindall & Cox, 8, Henrietta St., Covent Garden, W.C., state that the price of Mr. T. Thorne Baker's *The Spectroscope and Its Uses in General Analytical Chemistry*, published by them, and reviewed in *The Chemical News*, this vol., page 253 (April 20), is 8s. 6d., and not 7s. 6d. as originally given by them.



THIS list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

9522—Bakelite, Ges.—Manufacture of condensation products from phenols and aldehydes. April 6.

- 9405—Casale, I.—Synthetic production of ammonia. April 5.  
 9374—Farbwerke vorm. Meister Lucius Bruning.—Converting hydrocarbons, etc., into others containing a higher number of carbon atoms. April 5.  
 9369—Naugutuck Chemical Co.—Manufacture of diphenylguanidine. April 5.

#### Specifications Published this Week.

- 195113—Smythe, R. H.—Process to facilitate classification of mineral particles and to reduce losses in ore dressing by the aid of chemical substances.  
 173237—Westinghouse Lamp Co.—Process for the preparation of coherent masses of the rare metals and alloys and oxides thereof.  
 173757—Gerb-und Farbstoffwerke, H. Renner & Co., Akt-Ges.—Manufacture of salts of sulphonated coumarone resins.  
 195295—Pedemonte, A. L.—Manufacture of pure alumina.

#### Abstract Published this Week.

- 193200—Chlorinating organic compounds.—Boake, Roberts & Co., Ltd., Carpenters Road, Stratford, London, and Silberrad, O., Silberrad Research Laboratories, Buckhurst Hill, Essex.

The chlorination of organic compounds, more particularly of such compounds as are chlorinated with difficulty by ordinary methods, is carried out by means of sulphuryl chloride in conjunction with aluminium chloride and sulphur chloride. The last reagent may be omitted if substances, such as sulphur and carbon bisulphide, capable of yielding sulphur chloride under the conditions of reaction are present. An example describes the chlorination of p-dichlorobenzene to yield tetrachlorobenzene with lesser amounts of tri-penta- and hexachlorobenzene. The chlorination of anthraquinone, indanthrene, and naphthalene and its derivatives is also referred to.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the price of 1s. 6d. each.

#### PAMPHLETS.

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# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3291.

## NOTES ON THE INDIAN INDUSTRIAL REVIVAL.

It is apparent from the various pieces of news received that India is undergoing a revival on a large scale in the chemical industry. Some idea of this progress will be gathered from the following notes, compiled from authoritative sources:—

*Bengal.*—Dr. Bose's Laboratory, Ltd., have erected a plant at Belliaghata for the extensive production of sulphuric acid. The plant is of the S. Carves type, and manufactures 7 tons per day. The company anticipate an output of hydrochloric and nitric acids later. At Kumardhubi, large fireclay and silica works have just arrived at completion, drawing their material from adjacent deposits. A process for the manufacture of glass from an anhydrous sodium sulphate present locally has been adopted by the Belliaghata Glassworks, and this will render output more cheap and of better quality.

*Bombay.*—Mr. C. B. Amoula and Dr. A. N. Meldrum have experimented in the manufacture of rennet casein (*Journ. Indian Indus. Lab.*, 1923, III. (i), 95), and more than 22 cwts. have been transported to England for the determination of its commercial value.

*Central Provinces.*—At Wardha, a new feature is presented by Messrs. Ranade & Co., who are producing a red oxide paint of high quality.

*Madras.*—The Godavari and Kistna districts are under examination for the production of sodium carbonate and the general utilisation of alkaline deposits. Dr. Marsden, the industrial chemist for the Presidency, has issued his report and opinions for Government consideration. The factories under construction for the Kerala Soap Institute, Calicut, should be completed in May, and its gross profits are estimated at Rs. 12,500 per-annum.

*United Provinces.*—The proprietor of the Nawab Sugar Factory at Shahabad (Hardoi District) is in negotiations for the purchase of an up-to-date sugar refinery, and the termination of the deal will furnish a long-felt want. The Shr-Waha Lakshmi Sugar Corporation (Kheri District) has followed suit,

and is cultivating adjacently on a wide commercial basis. Applications and representations have been made for the formation of a new company called "The Lyallpur Sugar Co., Ltd., Cawnpore," with the considerable capital of five lakhs of rupees.  
J.M.

## A STUDY IN RHYTHMIC SERIES OF CHEMICAL CHANGES.

By K. C. VIRARAGHAVA, M.A.

The phenomenon of the appearance of one of the products of a reaction in a homogeneous or heterogeneous system, in a periodic instead of a continuous manner, has been noted in many cases, and the classical Liesegang phenomenon is the most studied. Various authors have interpreted it differently. There are the super-saturation theorists, adsorption advocates, and electrolyte coagulationists.

A gel is not essential for the production of this phenomenon. When aspirin is heated just to its melting point and allowed to cool, it solidifies in the form of concentric rings round a circular centre, the thickness of the rings gradually increasing from the centre outwards. Nor is the phenomenon confined only to a solid, or liquid, or their combined phase.

A series of experiments, "on the formation of the rhythmic bands by the interaction in narrow tubes of such gases as ammonia with hydrogen chloride, hydrogen bromide and hydrogen fluoride; and hydrogen sulphide with chlorine or sulphur dioxide, has been described by Koenig.

The typical rhythmical reactions so far studied are as follows:—

### HOMOGENEOUS SYSTEMS.

- (a) The evolution of carbon monoxide by the action of sulphuric acid on formic acid.
- (b) The evolution of carbon dioxide from super-saturated solutions.
- (c) The action of nitric acid on a mixture of sulphuric acid and formic acid.
- (d) Super-saturated sodium thiosulphate and alum solutions.
- (e) The solidifying of melted aspirin.

### HETEROGENEOUS SYSTEMS.

(a) *Involving the alternate formation and decomposition of a protective film.*

- (1) The decomposition of hydrogen peroxide in the presence of a clear film of mercury.

(2) The interaction of calcium carbonate and acetic acid.

(b) *Involving slow diffusion.*

(1) Silver chromate in gelatin.

(2) Lead chromate or iodide in agar.

(3) Lead carbonate in silicic acid.

(4) Interaction of mercurous nitrate and sodium formate in agar.

(5) Hydrochloric acid with sodium chloride in gelatin.

The reactions which take place on some such base as a gelatin or agar-agar layer, are very complete. The concentration of the reacting solutions, temperature, light, impurities, *e.g.*, chlorine, the method of preparing the gel, the age and nature of the gel, peptisation, all influence the course of the reactions.

In all these reactions diffusion plays an important part, for instance, in the Liesegang phenomenon potassium chromate or dichromate must have been distributed in the gel and must have reached a certain equilibrium when the sol had set. When new forces are set up, *e.g.*, by introducing silver nitrate, equilibrium is upset, and counter influences are at work between silver ion and chromate radical. It is not known if the chromate ion exists, but certainly silver chromate is precipitated. Silver chromate is seen when silver nitrate solution is added to the gel. What, then, diffuses? If it is silver nitrate, it must pass through the ring of silver chromate, like copper ferro-cyanide in a porous pot. Silver chromate will then function as a semipermeable membrane in the gelatin structure. H. M. Fischer and D. McLanglin have found that all substances which give satisfactory Liesegang rings are impermeable toward molecularly dissolved substances and consequently it would seem unlikely that after the formation of the first ring a second and third ring could be formed.

It has been said that the chromate also diffuses. Only as a resultant of the diffusions of chromate and nitrate is the precipitate formed in periods. In an experiment the lower portion of a gel was completely deprived of its chromate before the reaction completed.

Hugh McGuigan has observed that the chromate is fixed, and remains so, unless an attraction force is exerted. The silver nitrate wanders on through the ring into the clear zone until it is sufficiently close to the chromate gelatin to exert an attraction which again draws the chromate and forms

another ring and clear zone. At the same time the chromate exerts a pull on the silver, and the ring is formed where the forces are balanced.

Dr. J. N. Friend has put forward the suggestion that colloidal silver chromate is first formed and the organic emulsoid gelatin retards the rate of precipitation, but all the same, diffusion continues until the colloidal particles have grown too large and then begin to precipitate out. He considers that the distance between the rings is therefore the algebraic sum of the rates of diffusion and precipitation. Dhar and Chatterjee have observed that peptisation is an important factor in the phenomenon of periodic precipitation. Possibly the insoluble silver chromate is in a finely dispersed state, and as they go on diffusing, they grow in size and precipitate out. But Williams and Mackenzie have experimental evidence to infer that silver chromate did not function as a protected colloid with a slow rate of diffusion, and diffused only like a crystalloid. The precipitation followed the usual rules of solubility product.

With regard to circular disposed precipitation, W. Moeller concluded that the structure of the gel is the main factor. Gelatin jellies contain two substances, one of which,  $\alpha$ -gelatin, forms a structural network and the spaces in this are occupied by  $\beta$ -gelatin, which is structureless. Rhythmic changes in the structure of the fibrillar network are suggested to be responsible for the separation of foreign substances in rhythmically distributed layers. According to him, Liesegang rings are not dependent on chemical interaction of substances after diffusion through a jelly medium. Forces are called into play which indirectly determine a rhythmical alternation in the coagulation of the dispersed phase.

But Prof. H. T. Brown believes that two opposing diffusive streams of reacting substances produce a rhythmical series of zones and bands which follow the contours of surfaces of equidensity. Apparently all bands contain particles of the same density. The size of the particles may also differ between the bands, and the differentially deposited particles might show colour differences. It has been said that the colour of dispersoids differs with the size of the particles.

In many of my experiments the rings came out with intervals in a regular rhythmical manner, but, after some time, beyond the range of the rings but contiguous

to them, several bands in thin films were deposited continuously with different colours. It has been observed that, when the concentration of the two reagents approximate to equality, the precipitate appears to be continuous, but under the microscope it is seen to be finely banded. Even with the naked eyes, the alternate-coloured continuous bands can be seen on the gelatin layer. Possibly, when there is the difference in concentration, the rings appear and at the stage when the concentrations equalise, the precipitate is formed in a continuous manner. The different colours need to be explained.

The suggestion has already been made that the existence of quanta is not limited to energy alone. Just as matter has been considered for centuries to be discontinuous it may be its reactions, too, are of a similar nature.

#### THE SIGNIFICANCE OF THE EXPERIMENTALLY DETERMINED CRYSTAL STRUCTURES OF THE ALKALI POLYHALIDES.

By GEORGE L. CLARK.<sup>1</sup>

*Jefferson Physical Laboratory, Harvard University.*

By means of a new and powerful method of X-ray analysis the crystal structures of some of the alkali polyhalides have just been determined by the writer in association with Professor William Duane. Both the details of the method and of the analyses have been presented in other notes.<sup>2</sup> It is the purpose of this note to bring the new experimental data to bear upon the great uncertainty concerning the real constitution of these unique compounds which has prevailed since their discovery 30 years ago by Wells and Wheeler.<sup>3</sup>

Few experimental facts concerning the alkali polyhalides have been known up to the present time, except that solutions of cesium iodide, for example, are able to dissolve iodine, or bromine or chlorine, and produce crystals whose chemical analyses may be expressed by the empirical formulae  $CsI_3$ ,  $CsI_5$ ,  $CsIBr_2$ ,  $CsBrI_2$ ,  $CsICl_2$ ,

$CsIBrCr$ , etc. Wells and Penfield<sup>4</sup> found that the trihalides crystallise similarly and may even be isomorphous. Stability measurements by the writer and by Ephraim<sup>5</sup> show that the trihalides form a remarkable continuous series, in which maximum dimensions of the atoms are favourable to stability: thus  $CsI_3$  is most stable, while  $CsCl_3$ ,  $KBr_3$  or  $NaI_3$  do not exist; and  $KI_3$ ,  $RbBrI_2$  and  $CsBr_3$  are all equally stable. These measurements also indicate very clearly that all salts which contain iodine form one stability and crystallographic series, and those containing bromine in the absence of iodine another; in other words, the heaviest halogen atom has a defining influence, so that such a formula as  $CsBrI_2$  might more properly be written  $CsI.BrI$ .

It has been suggested that in the alkali polyhalides the metal may have a higher primary valence, as is true of gold (which is in the same periodic group as the alkali metals) in the known reaction  $Au + Cl + Cl_2 = Au^{+++}Cl_3$ . Again, it has been advocated by Remsen,<sup>6</sup> Wells and Penfield,<sup>4</sup> McCombe and Reade<sup>7</sup> (in February, 1923), and others, that one or more of the halogen atoms have a higher valence than is true in the simple halides. Several experimental facts disprove these contentions. Freezing point and conductivity experiments show that the ions in a solution of  $CsI_3$ , for example, are  $Cs^+$  and  $I_3^-$ . This means that in a molecule of the trihalide the single primary valence bond which holds cesium and iodine together in  $CsI$  is unchanged, but that the iodide ion is able to associate with itself two additional atoms of iodine, or a halogen molecule capable of independent existence, and form complexes. In solution the equilibrium between  $I^- + I_2$  and  $I_3^-$  is very definitely established. Besides the complex anions of the halogens, those of sulphur,  $S_2S^{--}$ ,  $S_3S^{--}$ ,  $S_4S^{--}$ , and  $S_5S^{--}$ , have been identified by Küster,<sup>8</sup> and those of tellurium,  $TeTe^{--}$  and  $Te_3Te^{--}$  in the beautiful work of Kraus.<sup>9</sup> These are all manifestations of secondary

<sup>4</sup> Wells and Penfield, *Amer. J. Sci.*, 1892, XLIII., 21, 475.

<sup>5</sup> Ephraim, *Ber. deut. chem. Ges.*, 1917, L., 1,069.

<sup>6</sup> Remsen, *Amer. Chem. J.*, XI., 291.

<sup>7</sup> McCombe and Reade, *J. Chem. Soc.*, 1923, CXXIII., 141.

<sup>8</sup> Küster, *Zs. anorg. Chem.*, 1905, XLIII., 53; 1905, XLIV., 431; 1905, XLVI., 113.

<sup>9</sup> Kraus, *J. Amer. Chem. Soc.*, 1922, XLIV., 1,216.

<sup>1</sup> National Research Fellow.

<sup>2</sup> Clark and Duane, *Proceedings U.S. Acad. Sci.*, 1922, VIII., 90.

<sup>3</sup> Wells and Wheeler, *Zs. anorg. Chem.*, 1892, I., 442.

valence just as truly as the combinations of water with salts to form hydrates or of ammonia to form ammines (cationic complexes) are secondary valence phenomena. These experiments, however, cannot explain the structure and the real nature of these complex groups, and they cannot be interpreted so as to give concrete knowledge of secondary valence. The actual

crystal structures give this information unmistakably, and in addition answer many questions which are confronting chemists, such as whether or not the identity of the single chemical molecule is retained in the space lattice of a solid.

The crystal structures of four alkali polyhalides have now been more or less completely determined. The results are as follows:

KI <sub>3</sub> monoclinic	$d_{100} = 4.70 \times 10^{-3}$ cm.
CsI <sub>3</sub> orthorhombic	$d_{100} = 4.49$ , $d_{010} = 6.43$ , $d_{001} = 7.02 \times 10^{-3}$ cm.
CsIBr <sub>2</sub> rhombohedral	$d_{100} = 4.26$ , $d_{010} = 5.91$ , $d_{001} = 6.90 \times 10^{-3}$ cm.
CsICl <sub>2</sub> rhombohedral hexagonal $d$ (Cs to I along trigonal axis)	$= 6.102 \times 10^{-3}$ cm.

Of these, the first three have been studied by the writer<sup>2</sup> and the last by Wyckoff.<sup>10</sup> In spite of the fact that three crystallographic systems are represented, the exceedingly interesting result comes out that all four crystal structures present precisely the same relative arrangement of atoms in the unit parallelepiped, if these unit cells are properly oriented so as to include one molecule. It is of secondary importance for the purpose in hand that the unit cell planes may be perpendicular or inclined to each other, or that the axes may be equal or unequal in length. This arrangement is as follows: metal atoms at the corners of the cell, and halogen atoms inside the cell in a line on the body diagonal, with the heaviest halogen atom at the centre and the other two on the diagonal on either side equidistant from the centre (if they are alike). In CsI<sub>3</sub> and CsIBr<sub>2</sub> the distance from the centre along the diagonal of the two iodine or two bromine atoms is half that from the centre to the corner; hence the co-ordinates are  $(a/4, b/4, c/4)$  and  $(-a/4, -b/4, -c/4)$ , where  $a$ ,  $b$ , and  $c$  are the edge lengths of the unit cell in three directions at right angles. In CsICl<sub>2</sub> the chlorine atoms have a parameter of 0.19 of the total length of the diagonal on either side of the central iodine atom, so that the unit cell is a rhombohedron instead of a rectangular parallelepiped. It is an interesting conjecture whether the orthorhombic variety of CsICl<sub>2</sub>, if it does exist, is produced by a displacement of the chlorine atoms farther along the diagonal from the centre. The only other possibility would be that a chlorine atom occupies a central position instead of the iodine, but this

should be very much less stable than the other arrangement. There is no doubt but that the normal tendency of the compound is to form the rhombohedral hexagonal form.

In KI<sub>3</sub> the unit cell is a monoclinic prism which has been formed by the slight deformation of a cube. The parameter of the two non-central iodine atoms on the body diagonal is slightly less than 0.25 (approximately 0.23) of the total length of the diagonal.

Thus in every case experimentally observed the three halogen atoms are closely associated together in a line, and constitute a singly acting group in the space lattice just as truly as they do in the formation of complex anions in solution, and just as truly as the identity of the complex cation  $[\text{Ni}(\text{NH})_6]^{++}$  is perfectly maintained in the space lattice of crystals, as proven by the crystal structures of nickel halide and nitrate hexamminates determined by Wyckoff.<sup>11</sup> There is every reason to believe that the facts discovered for the four typical polyhalides are also true of all other polyhalides, since they are so closely related crystallographically and chemically. At least it is practically certain that the relative arrangement of atoms in the unit cells is the same. The experimental proof that the heaviest halogen atom is central in the halogen group is entirely compatible with the facts also experimentally observed that salts containing iodine form one stability and crystallographic series and bromine another. Differences in the polyhalides therefore arise only in the size and

<sup>10</sup> Wyckoff, *Ibid.*, 1920, XLII., 1,100.

<sup>11</sup> Wyckoff, *Ibid.*, 1922, XLIV., 1,239, 1,260.

shape of the crystal unit cell, and in most cases even the latter is the same.

While it is clear that the secondary valence group of the polyhalides, as well as those of amines and hydrates, maintains its individuality in the crystal space lattice, it is still a question whether the whole molecule of  $KI_3$ , for example, exists as such in the space lattice. It has been clearly demonstrated that the simple chemical molecule  $Na-Cl$  as it is found in vapour does not exist as such in the crystal lattice, since every sodium atom is surrounded at the corners of an octahedron by chlorine atoms, and every chlorine atom similarly by six sodium atoms. On the other hand, Bragg<sup>12</sup> has shown conclusively that the single molecules of organic substances, and perhaps of some inorganic compounds, are retained intact in the lattice, and that the actual symmetry of single molecules is the determining factor of crystallographic symmetry. Thus a single completely asymmetrical molecule in a unit cell can produce only the asymmetrical triclinic system; the higher symmetry of the monoclinic and orthorhombic systems is attained by placing 2 or 4 or 8 whole asymmetrical molecules in the unit cell properly oriented about planes or centres of symmetry. As a sort of middle ground between the lattices of sodium chloride and of organic compounds, there may be cited the examples of the hexamminates of the nickel halides<sup>11</sup> and the hexahydrate of zinc bromate.<sup>13</sup> In the single molecule of  $Ni(NH_3)_6Cl_2$ , six molecules of ammonia are bound to the nickel atom by secondary valence forces, and the two chlorine atoms by primary valence bonds. In the crystal lattice each nickel atom is still surrounded symmetrically by six ammonia molecules, but there are not two but eight equidistant chlorine atoms in the same way that there are six chlorine atoms around each sodium atom in sodium chloride. The compound  $Zn(H_2O)_6BrO_3$  is exactly analogous.

It cannot be denied that the forces which hold organic molecules fixed in crystal lattices, or which enable very long molecules lying parallel to form liquid crystals, or which cause the molecules of almost all organic substances to become very definitely oriented in surfaces, are the same kind of

forces which hold electrically neutral molecules of ammonia or water to metal atoms, either in the single molecule or in the crystal lattice. Now it has been proven that precisely the same thing is true of the halogen groups in polyhalides, even though the forces are holding together three atoms, or even more, of the same chemical nature, instead of grouping neutral atoms or molecules around a central atom of greatly different nature.

If planes are drawn through the lattices of the four experimentally studied trihalides so as to enclose  $1/2$  instead of one molecule, then the metal atoms and the heaviest (previously body-centred) halogen atoms appear alternately at the corners of the new unit, while one atom of iodine in  $KI_3$  or  $CsI_2$ , one atom of bromine in  $CsIBr_2$ , or one atom of chlorine in  $CsICl_2$  lies on the body diagonal at 0.46 or 0.50 or 0.38 of its length from a corner iodine atom. Hence the structures are remarkably closely related to the simple halide unit cubes. A halogen atom in the latter case is replaced by a polyhalide group. Dimensions are changed and perfect cubic symmetry destroyed, but every metal atom is surrounded by six complex halogen groups, each acting as a single point in the lattice. The single primary valence bond of the chemical molecule is split in the lattice, but the secondary valence group within itself is retained intact.

It has already been stated that the stability of the alkali polyhalides depends upon the metal—as a matter of fact relative stabilities are directly proportional to the atomic volumes of the metals. This is now easily explained. The size of the metal atom in the lattice determines the dimensions of the unit cell, or the interplanar distances, other things being equal. The smaller the dimensions the more difficult it is for three halogen atoms to lie on a straight line within the cell with any degree of stability. Halides of potassium are just able to form polyhalides; as a matter of fact only the iodide is able to form such compounds sufficiently stable to isolate. The size of the potassium atoms and the interplanar distances are such that upon the formation of  $KI_3$  the string of iodine atoms predominates, the frame-work of the potassium atoms is distorted unequally in different directions, and the resultant properties approximate those of elementary iodine crystals. The compound  $NaI_3$  does not exist because, even if the  $I_3$  groups were

<sup>12</sup> Bragg, *J. Chem. Soc. (London)*, Dec., 1922, CXXI., 2,766.

<sup>13</sup> Wyckoff, *Amer. J. Sci.*, 1922, IV., 188.



the exhibitors have, in the past, been Canadian and American firms.

These exhibitions should afford an opportunity of familiarising traders and consumers in Western Canada with the productions of U.K. firms. Arrangements have been made by the Dept. of Overseas Trade for participation by H.M. Trade Commissioner in Western Canada in the fairs to be held at Brandon, Edmonton, Regina and Vancouver in July and August.

At each a Bureau of Information will be maintained by H.M. Trade Commissioner, at which it is desired to display copies of leading U.K. trade and technical journals, particularly those dealing with agricultural and allied matters. The Trade Commissioner proposes not only to display such journals, but to distribute them in suitable quarters, and would therefore be glad to receive up to 50 copies each of journals dealing with agricultural implements and machinery (including stationary engines, tractors, dairy supplies and machinery, grinders, crushers and feed cutters, residential electric lighting plants, etc.), mining, engineering (including wire rope, pulleys, etc.), telephones, mechanics' tools for farm and workshop, municipal equipment, ships' fittings and ship chandlery, and marine engines; and about 20 copies of other trade journals.

#### CZECHO-SLOVAKIA'S EXPORTS FOR THE FIRST QUARTER OF 1923.

Following are the values exported according to class of goods during the period January to March:—

	Millions Kc.
Wood, coal and fuel .....	495
Sugar .....	352
Cotton, yarns, etc. ....	344
Wool and woollen goods .....	245
Glass and glassware .....	191
Iron and ironware .....	143
Corn, flour, malt .....	136
Leather and leather goods .....	63
Flax, jute, hemp .....	57
Paper and paper goods .....	54
Ready-made clothes .....	51
Earthenware .....	44
Chemicals and chemical products .....	32
Machines and apparatus .....	28
Minerals .....	30
Wooden ware .....	23
Imitation stones and goods thereof .....	28

The greatest increase took place in the export of wood and coal, which in March reached a total value of 187 million crowns. The textile industry also had a favourable month; cotton products of a value of 98 millions, and woollen goods of a value of 81 millions were exported. In spite of the difficult situation prevailing in the glass industry, the latter was able to export glassware to a value of 64 million crowns. The export of iron has been steadily increasing since the beginning of the year, and in January the export of iron and iron goods amounted to 34 million crowns; in February the export rose to 50 million crowns, and in March a further increase of 59 millions took place.

Germany and Austria again take first place as purchasers of Czech goods; no less than 40 per cent. of the total exports going to these countries in the first quarter of this year. England occupies third place with a total of 282 million crowns.

#### TOWN REFUSE AS MANURE.

The Ministry of Agriculture and Fisheries has just issued a leaflet drawing the attention of farmers and others to substitutes for stable manure, which is now becoming very scarce. Among the various possibilities is to be reckoned ashpit refuse, which is available in large quantities but is at present used to a very limited extent. Town authorities are now disposing of their refuse in a better way, and some are adding other wastes and crushing the whole for use as a fertiliser.

The amounts of ashpit refuse available over the country are very large. It is estimated that no fewer than 10,000,000 tons per annum are produced in England and Wales, while in London alone the production is estimated at 1,500,000 tons per annum. Broadly speaking, town refuse has given successful results in two cases:—

(a) On heavy-land farms or allotments, where it is used for root crops, cabbages, &c.;

(b) For raising the level of low-lying wet ground and forming new land which can be used for allotments.

Considerable quantities of town refuse have been used by farmers on the heavy London clay soils of the Home Counties. About 10 tons per acre is a usual dressing; it should be spread before the winter ploughing begins so that it can be well

worked into the soil. It then lightens the stiff soil and facilitates cultivation generally, and good root and other crops are usually obtained. Farmers round some of the larger Scottish towns, *e.g.*, Glasgow, Dundee, Perth, and Aberdeen, use considerable amounts, probably even more than those round London. Uncrushed refuse is sold from Dundee, where the demand is stated to be greater than the supply: the 1921 deliveries are said to have been 39,000 tons.

There are six types of refuse sent out from towns:—

1. "Dry" refuse: the contents of refuse bins and "dry" ashpits.

2. Separated dust: finely divided material separated mechanically from the dry refuse through a  $\frac{3}{8}$  in. or  $5/16$ ths in. sieve.

3. "Mixed" refuse: the contents of privy middens and ash closets.

4. Night soil: the contents of pails containing crude faecal matter only; this is produced in towns where the pail system is used. When dried and granulated it contains some  $5\frac{1}{2}$  per cent. nitrogen,  $5\frac{1}{2}$  per cent. phosphates, and  $2\frac{1}{2}$  per cent. potash.

5. Mixed night soil.

Market and slaughter-house refuse are sometimes mixed with 1, 2, 3 and 5.

6. Street sweepings and other wastes.

Of these, street sweepings and unmixed night soils are well known to farmers, and are often easily disposed of. One large London district disposes of its street sweepings at 10s. per ton. Night soil in the dry form, unmixed with ashes, is now sold by a few corporations at about £7 per ton. If the methods used in these places were generally applicable to town and city conditions the problems arising out of the waste of sewage would be solved, and the shortage of organic manures on the farm would be greatly relieved.

In its crude form, asphalt refuse contains a small percentage of cans, bottles, &c., of no use on the farm but indeed constituting a nuisance. In the more progressive towns metals, cinders and bottles, for all of which a use or market can be found, are removed.

The material can be offered to farmers as it stands. Its composition, however, is not particularly good in spite of its smell. Improvement is effected by enriching with a certain amount of other waste matter, such as street sweepings, slaughterhouse refuse, and stable manure. Analysis indicates that these manures have the following approximate composition:—

	Per cent.
Organic matter .....	25—40
Nitrogen .....	0.4—0.6
Phosphoric acid ( $P_2O_5$ ) .....	0.3—0.5
Equivalent to tricalcium phosphate, $Ca_3(PO_4)_2$ .....	0.7—1.1
Potash ( $K_2O$ ) .....	0.3—0.5

In some northern towns it is found possible to add a considerable proportion of night soil in addition to street sweepings, cattle market manure, slaughterhouse refuse and stable manure. An excellent fertiliser is thus obtained, containing one or more per cent. of nitrogen.

The enrichment of the refuse is shown by the fact that the nitrogen content runs as high as 1 per cent., whilst the samples of unfortified town refuse contain only about 0.5 per cent.

It has been proposed to add soot to the town refuse, but this would not be a sound procedure.

These modern prepared wastes are well worth attention by farmers, and trial lots may usefully be put on the root and cabbage land, and possibly also used for hay on stiff clay soils.

#### REPARATION DYESTUFFS.

The Board of Trade desire to draw attention to the fact that under the Reparation Clauses of the Peace Treaty requisitions are made periodically for the delivery of certain German dyestuffs on reparation account. Information as to the requirements of colour users for dyestuffs which cannot be obtained from British manufacturers is collected by the Colour Users' Association and furnished periodically to the Board of Trade.

In order that this information may be as complete as possible, the Board would be glad if all users—whether members of the Association or not—would furnish particulars of their estimated requirements for German dyestuffs, say once every three months, to the Secretary, Colour Users' Association, Cromwell Buildings, Blackfriars Street, Manchester.

The Inventions Development (1923) Co., of Belfast, has been reorganised. It will continue to carry on its usual business and develop ideas and processes commercially.

The Federation of British Industries has sent a letter to H.M. Government on the question of Inter-Imperial Trade, and urging the early passage of the Empire Cotton Bill, which has been promoted with the intention of safeguarding the cotton industry.



### NEW CHILEAN LAW REGARDING THE SIZE OF JUTE SACKS USED IN THAT COUNTRY.

H.M. Chargé d'Affaires at Santiago, Chile, has reported to the Dept. of Overseas Trade that a law was passed by Congress and approved by the Council of State on the 9th February, limiting the size of jute sacks to be used in transport by human labour.

A translation of the law reads as follows:

Article 1.—The weight of any sack containing any class of product which has to be carried by human labour (man handled) shall not exceed 80 kilogrammes. The contravention of this law shall be punished by a fine of 20 pesos for each infraction. This law will come into force 180 days after the date of its publication in the *Diario Oficial*.

Transitory Article.—The dispositions of this law will not affect articles which are already packed on the date on which it comes into force.

The measure was introduced into Congress with the object of protecting the workers in the nitrate industry, where the weight of a full sack of nitrate has been 92 kilos.

The importance of the new law lies in the fact that Jute nitrate bags form the chief article of importation into Chile, both as regards quantity and value. Unless it is found commercially possible to utilise the old 92 kilogramme sacks, the new law will therefore presumably result in orders for new jute sacks.

Messrs. Murphy & Sons, Bureau of Bio-Technology, have issued their *Bulletin* No. 9, Vol. II, (March), containing contributions on the following:—

*The "Biotec" Comparator.*

The Destruction of Structural Timber: its causes and prevention.

The Suppression of Insect Pests and Fungoid Diseases. The Fumigation of Commercial Glasshouses.

Nicotine Petroleum Emulsion.

Micro Organisms in the Leather Industries.

The May issue of *Current Opinion* contains a short but important article upon *The Need for Knowledge*. It is pointed out that very few people could pass a test in any subject outside their own calling, and indeed, few are familiar with the wider aspects of their particular industry or branch.

### DRUGS AND CHEMICALS FOR ROUMANIA.

Mr. Szana, British Vice-Consul at Timisoara, reports that a local firm is desirous of purchasing drugs and chemicals from British sources.

The name and address of the firm, together with further particulars, may be obtained by British firms upon application to the Dept. of Overseas Trade.

### WEATHER FORECASTS.

The Postmaster-General announces that arrangements have been made in conjunction with the Meteorological Department of the Air Ministry for weather forecasts to be distributed each afternoon to telephone exchanges. The forecasts will cover the period from 6 p.m. on the day of issue till 6 p.m. on the following day. These arrangements came into operation on May 1. The forecasts will be available between 5 p.m. and midnight each day on demand by telephone subscribers, and should be of especial benefit to farmers and other residents in rural areas.

Subscribers on rural party lines will receive the information free of charge, a local call fee being charged in the case of other subscribers. The forecasts may also be obtained by enquirers at call offices on payment of the usual call office fee.

In the April number of *The Journal of the Chemical Society*, pp. 881-884, DR. ALEXANDER SCOTT contributes a paper entitled *Isolation of the Oxide of a New Element A Correction*. Dr. Scott states that he submitted the sample of his pale buff-coloured powder ("New Oxide," as described in his communication to the Chemical Society on February 1, an account of which appeared in *The Chemical News*, Feb. 9, p. 81, to Drs. Coster and Hevesy for examination by X-ray spectral analysis. These authorities have failed to find any Hafnium lines in the oxide and in the original New Zealand sand from which Dr. Scott prepared the oxide.

The constituents appear to be oxides of iron, titanium, and traces of other metals all previously known.

Dr. Scott has unravelled the mystery of his results by further analyses, which seem

to indicate that he was dealing with a mixture of  $K_2TiF_6$  and other double fluorides, which would yield a mixture of oxides on ignition by his analytical procedure.

PROCEEDINGS AND NOTICES OF SOCIETIES.

THE ROYAL SOCIETY.

At the Ordinary Meeting on Thursday, May 3, the following papers were read:—

LEONARD HILL and A. EIDINOW. *The Influence of Temperature on the Biological Action of Light.*

The biological action of light is accelerated by warmth, retarded by cold. This is true for bacteria, infusoria and human skin. The temperature coefficient for infusoria, between  $1^\circ$  and  $20^\circ$  C., is about 3.0. By adequate exposure to cool air over-action of the sun on the skin can be prevented.

F. A. E. CREW. *Studies in Intersexuality. I.—A Peculiar Type of Developmental Intersexuality in the Male of the Domesticated Mammals.* Communicated by Prof. R. C. Punnett, F.R.S.

Papers read in title only:—

E. J. MORGAN and J. H. QUASTEL. *The Reduction of Methylene Blue by Iron Compounds.* Communicated by Prof. F. G. Hopkins, F.R.S.

1. The restoration of the power to reduce methylene blue to boiled milk by means of ferrous sulphate solution is shown to be due to the inorganic constituents of the milk.

2. It is shown that methylene blue is reduced by ferrous sulphate solution in the presence of sodium hydroxide, carbonate, bicarbonate or phosphate and of the sodium salts, such as acetic, tartaric or citric. Ferrous sulphate solution alone will not effect any perceptible reduction.

3. The reduction has been followed quantitatively with the result that it is clear that two ferrous molecules always react with one of methylene blue.

4. The mechanism of the reduction has been studied with a view to throwing light on the biological hydrolytic oxidation-reduction system. It is suggested that the clearest light is afforded by the considera-

tion of the relative affinities of the oxygen acceptor for the hydroxyl ion and of the hydrogen acceptor for the hydrogen ion.

C. F. COOPER. *The Skull and Dentition of PARACERATHERIUM BUGTIENSE. A Genus of Aberrant Rhinoceroses from the Lower Miocene Deposits of Dera Bugti.* Communicated by Dr. A. Smith Woodward, F.R.S.

W. L. BALLS. *The Determiners of Cellulose Structure as seen in the Cell Walls of Cotton Hairs.* Communicated by Dr. F. F. Blackman, F.R.S.

The use of plane and circularly polarised light and of immature hairs has enabled further observations to be made more easily. The reversals of the spiral fibrillar structure show their full number, as soon as the secondary wall is visible, indicating pre-determination thereof during growth in length. Thus far, however, the primary wall cannot be made to demonstrate such reversals visually; but on development of the pre-cellulose it shows instead a pair of opposed spirals whose pitch corresponds to that of the slip spirals of the secondary wall. These slip spirals are now found to be structurally connected with the quicker pit spirals and invariably opposed to the latter in direction; the tangents of their angles happen to stand in the ratio of 4:1, which suggests polymerisation from the pre-cellulose of the primary wall. The rotation of the plane of polarisation by a single layer of secondary cell-wall is inverted on opposite sides of a reversal point; thus the molecular structures of the right-hand and left-hand areas would seem to be mirror-images.

Attention is called to the low specific gravity of the cell-wall, explicable as a consequence of its spongy structure, and to the uncertainty of any existing determinations thereof. It is also pointed out that correct microscopic definition can only be obtained by the use of an analyser in the eye-piece.

Some tentative conclusions can be drawn, pending X-ray analysis, as to the probable space-lattice conformation of cotton and other celluloses, which bring one effectively to a modernised re-statement of Nägeli's micellar theory.

I. DE B. DALY. *The Influence of Mechanical Conditions of the Circulation on the Electro-cardiogram.* Communicated by Prof. E. H. Starling, F.R.S.

THURSDAY, MAY 10.

Papers read:—

PROF. A. FOWLER, F.R.S. *The Series Spectrum of Trebly-ionised Silicon. (Si IV).*

SIR ROBERT ROBERTSON, F.R.S., and W. E. GARNER. *Calorimetry of High Explosives.*

H. S. HOLE SHAW, F.R.S. *Stream line Filter.*

F. W. ASTON, F.R.S. *A Critical Search for a Heavier Constituent of the Atmosphere by means of the Mass-spectrograph.*

Papers read in title only:—

PROF. H. E. ARMSTRONG, F.R.S. *Electrolytic Conduction: Sequel to an attempt (1896) to apply a Theory of Residual Affinity.*

PROF. H. E. ARMSTRONG, F.R.S. *The Origin of Osmotic Effects. IV.—Hydrodynamic Change in Aqueous Solutions.*

R. W. WOOD, FOR. MEM. R.S., and A. ELLETT. *On the Influence of Magnetic Fields on the Polarisation of Resonance Radiation.*

W. G. PALMER. *A Study of the Oxidation of Copper and the Reduction of Copper Oxide by a New Method.* Communicated by Sir William Pope, F.R.S.

E. A. FISHER. *Some Moisture Relations of Colloids. II.—Further Observations on the Evaporation of Water from Clay and Wool.* Communicated by Prof. A. Smithells, F.R.S.

#### THE CHEMICAL SOCIETY.

At the meeting on Thursday, May 10, the Bayer Memorial Lecture was delivered by PROFESSOR W. H. PERKIN, LL.D., F.R.S., in the Lecture Hall of the Institution of Mechanical Engineers, Westminster.

#### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

ORDINARY MEETING.

Mr. P. A. Ellis Richard, President, in the chair.

A Certificate was read for the second time in favour of Mr. Robert C. Grimwood, A.C.G.F.C., D.I.C., A.I.C.

The following were elected Members of the Society: Messrs. John Myers, F.I.C., John Loudon Buchanan, F.I.C.

The following papers were read:—

*The Quantitative Determination of Hemp and Wood in Papers containing these two Fibres*, by WILLIAM DICKSON, F.I.C.

The author considers that in the microscopical determination of hemp fibres in the presence of wood, examination alternately by ordinary and polarised light enables one to readily distinguish the microstructure of the different fibres. He has devised a method for quantitative work utilising the counting method of Spence and Krauss *World's Paper Trade Review*, 18th Dec., 1917.

The paper is disintegrated by boiling with dilute caustic soda and the pulp churned up with an egg switch. The fibre is then stained by Cross and Bevan's double malachite green and congo red method, well spread out on the cover slip and mounted in the usual way. The counting is done by Spence and Krauss's method, but no correction factor is required to convert proportions by diameter into proportions by dry weight of furnish.

*The Estimation of Fat, Lactose, and Moisture in Dried Milks*, by H. JERICOTT, M.Sc., F.I.C.

As a result of examining over 25,000 samples of dried milk, it is contended that (1) Moisture is best determined by drying at 102-103° C. for 1 to 2 hours; (2) Fat can most satisfactorily be determined by a careful use of the Werner-Schmidt method. A modified Gerber method gives less accurate but concordant results for rough routine purposes; (3) The polarimetric determination of lactose in milk powders, whilst offering certain advantages, should not be used where great accuracy is desired. In such cases a gravimetric process, based upon the modified Fehling's method of Quisumbing and Thomas, is recommended.

*The Determination of Lactose by the Polarimetric and Gravimetric Method*, by A. L. BACHARACH, B.A., A.I.C.

Pure  $\alpha$ -lactose mono-hydrate was prepared by careful recrystallisation and drying. It was shown to have the value for

$[\alpha]_D^{20}$  of 52.42, agreeing with the most trustworthy recorded figure.

The reducing power of pure  $\alpha$ -lactose monohydrate was also determined by the modification of the Fehling method due to Quisumbing and Thomas. The accuracy of this method claimed by these authors was confirmed, but the reducing power obtained was somewhat higher, 0.1000 gm. of lactose hydrate giving 0.1565 grm. of cupric oxide.

*The Melting Point and Iodine Value of Refined Natural D-Camphor*, by MAURICE S. SALAMON, B.Sc.

The iodine value and melting point of specially purified d-camphor have been re-determined, and it is shown that the usually accepted value is too high, and that that the usually published melting point is too low. The iodine value of the specially refined d-camphor is found to be 0.1, and the melting point 179° C. It is concluded that the majority of previous determinations must have been made on d-camphor that was slightly impure.

The iodine value of oil of camphor has also been re-determined, and examples are given of how this value, together with the melting point and iodine value of d-camphor can be used to indicate the percentage of camphor present in a sample of refined d-camphor. This suggested that refined d-camphor for pharmaceutical purposes should have a melting point not lower than 176° C. and an iodine value of not more than 0.7.

*The Presence of Barium and Strontium in Natural Brines*, by A. G. FRANCIS, B.Sc., F.I.C.

The results of the analysis of 7 samples of brines from deep boreholes in Derbyshire, Staffordshire, and Scotland are recorded together with a brief account of the method of analysis adopted. The maximum quantities of barium and strontium chlorides found were 178.2 and 169.4 parts per 100,000 respectively.

An explanation based upon the "permutit" reaction is put forward to account for the presence of chlorides of barium and strontium in natural brines, and it is shown that there is a gradation in the strengths of sodium chloride solutions necessary completely to remove calcium, strontium and barium from a "permutit"-filter charged with these elements.

## THE GEOLOGICAL SOCIETY.

At the meeting on April 18, 1923, Prof. A. C. Seward, Sc.D., F.R.S., President, and, afterwards, Dr. Herbert H. Thomas, M.A., Vice-President, in the chair, the list of donations to the library was read; it included, among others, the following works: Imperial Institute, Monographs on Mineral Resources, with special reference to the British Empire: Copper-Ores, by Robert Allen, 1923; Mercury-Ores, by Edward Halse, 1923; Memoirs of the Geological Survey of England and Wales, Explanation of Sheet 169—The Geology of the Country around Coventry, including an account of the Carboniferous Rocks of the Warwickshire Coalfield, by T. Eastwood, W. Gibson and others, 1923; and Memoirs of the Geological Survey, Special Reports on the Mineral Resources of Great Britain—Vol. XXV.: Lead- and Zinc-Ores of Northumberland and Alston Moor, by Stanley Smith, 1923; and Vol. XXVI.: Lead- and Zinc-Ores of Durham, Yorkshire, and Derbyshire, with Notes on the Isle of Man, by R. G. Carruthers and Sir Aubrey Strahan, 1923.

The following communication was read: *The Structure of the Bowmore-Portaskaig District of Islay*, by JOHN FREDERICK NORMAN GREEN, B.A., F.G.S.

Microscope-sections and rock-specimens from the Bowmore-Portaskaig district of Islay were exhibited in illustration of this paper.

At the meeting held on Wednesday, May 2, a lecture was delivered by Prof. JOHN JOLY, D.Sc., F.R.S., F.G.S., on *The Bearing of some Recent Advances in Physical Science upon Geology*.

## ROYAL SOCIETY OF ARTS.

On Wednesday, May 9, at the Ordinary Meeting, a lecture entitled *Surface Combustion—with special reference to Recent Developments in Radiophragm Heating*, was delivered by WILLIAM ARTHUR BONE, D.Sc., Ph.D., F.R.S., Professor of Chemical Technology, Imperial College of Science and Technology, South Kensington. Mr. D. Milne Watson, M.A., LL.B. (Gas Light and Coke Company) presided.

An experimental demonstration of "Radiophragm" Heating was given by Mr. F. J. Cox, M.Inst.M.E.

### THE INSTITUTION OF ELECTRICAL ENGINEERS.

At the Ordinary Meeting in the Lecture Theatre, on Thursday, May 10, the Faraday Medal was presented to the Hon. Sir Charles A. Parsons.

The fourteenth Kelvin lecture, entitled *Problems in Telephony, Solved and Unsolved*, was delivered by Dr. J. A. FLEMING, F.R.S., Honorary Member.

### INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The seventy-first general meeting was held at the house of The Royal Society of Arts on Tuesday, May 8. A paper entitled *Heavy Grade Egyptian Crude Petroleum*, was read for W. A. GUTHRIE, F.I.C., F.R.S.E., M.Inst.P.T., &c. H. Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst.Mar.Eng., presided.

### THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

#### PASS LIST FOR THE APRIL EXAMINATIONS, 1923.

The following Associate has passed the examination for the Fellowship:—

In branch G: Chemical Engineering: Grisenthwaite, Arthur Turner, A.C.G.F.C., B.Sc. (Lond.).

The following candidates have passed the examination for the Associateship:—

In General Chemistry: Brady, Peter Joseph, East London College; Grayson, Harold John, University College, London; Gregory, Louis Wilfred, University College, Nottingham; Loasby, Geoffrey, B.Sc. (Birmingham), Birmingham University; Marison, Leslie William, East London College; Player, Harold William Victor, King's College, London; Smith, Daniel Agnew, University College, Nottingham; Vineall, George John Charles, B.Sc. (Lond.), University College, Southampton

Seven candidates failed to satisfy the examiners.

### THE INSTITUTE OF METALS.

The thirteenth annual May Lecture of the Institute of Metals was delivered on

Wednesday, May 2, at Storey's Gate, Westminster, by Dr. W. ROSENHAIN, F.R.S., of the National Physical Laboratory, who chose as his subject, *The Structure of Alloys*.

Referring to the great accumulation of facts in regard to the properties and micro-structure of alloys which have been forthcoming in recent years, the lecturer said that the time had arrived when it was most desirable that there should be found a key to this maze of knowledge in the form of a general theory that would link together the mass of facts into a homogeneous whole. Such a theory he attempted to put forward, basing it upon the intimate knowledge of crystal structure which had recently been acquired by means of the application of X-rays to the study of the arrangement of atoms in crystals. The crystal structures found in pure metals became modified in the case of alloys, particularly in those called solid solutions, where a second kind of atom, the atom of the alloying element, entered into the structure of the crystal and produced in it certain minute changes. With regard to such changes the lecturer put forward two simple principles, and was then able to show a striking series of inferences from his theory, which accorded closely with a large number of experimental facts. Connections between various series of properties in metals and their alloys were established which had not formerly been recognised, such as the relation between hardness and alloying power. Especially important is the connection between the minute distortion of crystal structure which occurs in alloys and their behaviour on melting and freezing, while such phenomena as plasticity, diffusion and others fell easily into line with the same type of explanation. Most important of all, perhaps, is the fact that this new theory of alloy structure affords a ready explanation of the electrical properties of metals and alloys and the changes of those properties when the metal is heated or cooled. These explanations cover the mysterious phenomena of super-conductivity found in many metals when cooled nearly to the absolute zero of temperature.

### ROYAL INSTITUTION.

On Tuesday, May 8, PROFESSOR A. C. SEWARD began a course of two lectures on *Ice and Flowers of Greenland*, and on

Thursday, May 17, PROFESSOR COKER delivers the first of two lectures on *Engineering Problems solved by Photoelastic Methods*.

The Friday Evening Discourse on May 11 will be given by PROFESSOR W. A. BONE on *Gaseous Combustion at High Pressures*, and on the 18th by MR. W. M. MORDEY on *Studies in Alternating Magnetism*.

SIR ERNEST RUTHERFORD'S postponed discourse will be given on Friday evening, June 15, and his concluding lecture on *Atomic Projectiles* on Saturday afternoon, June 16.

The Annual Meeting of the members of the Royal Institution was held on Tuesday afternoon, May 1, Sir James Crichton Brown, Treasurer and Vice-President, in the chair. The Annual Report of the Committee of Visitors for the year 1922, testifying to the continued prosperity and efficient management of the Institution, was read and adopted. The Report of the Davy Faraday Research Laboratory Committee was read. Sixty new members were elected in 1922, and 63 lectures and 19 evening discourses were delivered. The books and pamphlets presented amounted to about 162 volumes, making, with 426 volumes (including periodicals bound) purchased by the Managers, a total of 588 volumes added to the library in the year. Thanks were voted to the President, Treasurer and Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year. The following were unanimously elected as officers for the ensuing year:—

*President*, The Duke of Northumberland.

*Treasurer*, Sir James Crichton-Browne.

*Secretary*, Sir Arthur Keith.

*Managers*, Sidney G. Brown, John Mitchell Bruce, Sir Dugald Clerk, John Ambrose Fleming, Sir Richard Glazebrook, Earl Iveagh, Sir Alexander C. Mackenzie, Robert Mond, Sir Edward Pollock, Alfred W. Porter, Lord Rothschild, Sir David Salomons, William Stone, Sir Alfred Yarow, the Right Hon. Lord Justice Younger.

*Visitors*, Sir Harry Baldwin, William A. Bone, Alfred Carpmael, Ernest Clarke, Edward Dent, Thomas W. Dewar, George H. Griffin, W. E. Lawson Johnston, Colonel F. K. McClean, Sir Malcolm Morris, W. Rushton Parker, Walter Peacock, Major C. E. S. Phillips, Hugh Munro Ross, Sidney Skinner.

#### FUTURE LECTURES.

Friday Evening Discourses, addressed to members and their friends at 9 p.m.

May 11: WILLIAM ARTHUR BONE, D.Sc., F.R.S., M.R.I., Prof. of Chemical Technology, Imperial College, *Gaseous Combustion at High Pressures (New Experiments)*.

May 18: WILLIAM MORRIS MORDEY, PAST PRES.I.E.E., M.INST.C.E., M.R.I., *Recent Studies in Alternating Magnetism (with Experiments)*.

May 25: SIR ASTON WEBB, K.C.V.O., C.B., President of the Royal Academy, *The Development of London*.

June 1: PROF. HENDRIK ANTOON LORENTZ, HON.F.R.S., HON.M.R.I., PH.D. Haarlem University, *The Radiation of Light*.

June 8: MISS JOAN EVANS, B.LITT. (OXON.), F.R.I., Member of Council, St. Hugh's College, Oxford ("Magical Jewels," Clarendon Press), *Jewels of the Renaissance*.

Tuesdays, May 22, 29, June 5: *Discoveries in Egypt*, by W. M. FLINDERS PETRIE, D.C.L., LITT.D., F.R.S., etc., Prof. of Egyptology, University of London.

Thursdays, May 17, 24: *Engineering Problems Solved by Photoelastic Methods*; 1 (1) *Improvement in Apparatus*, (2) *Contact Pressures and Stresses*; 2 (1) *The Testing of Materials*, (2) *The Action of Cutting Tools*. By E. G. COKER, D.Sc., F.R.S., M.INST.C.E., M.R.I., Prof. of Engineering, University of London.

Thursdays, May 31, June 7: *The Nature of Enzyme Action*, by SIR WILLIAM M. BAYLISS, LL.D., D.Sc., F.R.S., Prof. of General Physiology, University College, London.

Saturdays, June 2, 9: 1, *The Vegetation of the Andes*; 2, *The New Zealand Flora*, by ARTHUR W. HILL, Sc.D., F.R.S., Director of the Royal Botanic Gardens, Kew.

#### CORRESPONDENCE

##### MAKING COLOUR MAKERS.

*To the Editor of THE CHEMICAL NEWS.*

SIR,—Professor Perkin, of Leeds University has just announced that no fewer than forty-seven students have gone out this year from the Departments of Colour Chemistry and Dyeing, of which he is the head, to take up positions with colour makers, wool dyers, cotton dyers, calico printers, artificial silk manufacturers, and

in other industries. It is heartening news to those who believe, as I do, that British industry depends to-day, and is in the future going to depend more and more, upon the pooling of scientific knowledge won at our universities and the technical ability which can be acquired only from large-scale production.

In these circumstances it is not quite clear on what Professor Perkin bases his fear that, even yet, the artificial dyestuffs industry might one day become "moribund" in this country. At the present moment both colour makers and colour users are practically unanimous in their determination that a national dyestuffs industry shall be maintained and developed in Great Britain; differences between them there are, but they are differences regarding not the end to be attained, but the means to attain it.

There has been a considerable amount of prejudice to be overcome in securing the widest use of British made dyes; but that is an inherent tendency which is gradually and successfully being lived down by British makers. Makers and users realise that they must work hand in hand, and it is an excellent augury for a continuance of amicable feeling that during the Ruhr crisis no attempt has been made to increase prices. Before the war we depended on Germany for eighty per cent. of our dyestuffs; to-day we can supply more than eighty per cent. of the dyes required by British colour users. It is a considerable achievement, and it gives promise in the future of offering many more than Professor Perkin's estimate of twenty openings a year to students qualified in colour chemistry.

I am, Yours, etc.,

W. J. U. WOOLCOCK,

The Association of British Chemical  
Manufacturers, 166, Piccadilly,

London, W.1.

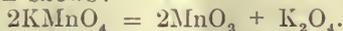
27th April, 1923.

#### POTASSIUM PERMANGANATE APPLICATIONS TO ENCOECARIA AGALLOCHA.

Two bleach methods have been tried with evident success, both of which call for the co-operation of sulphurous acid as a decoloriser. The first method produced a wood almost of pure whiteness; the second showed a slight brownish tinge not altogether out of keeping with modern match manufacture.

The usage of neutral potassium permanganate constitutes the first process. The *gangwa* is chipped into sticks 4.5 cms. in

length, having an approximate cross-sectional area of 4 sq. mm., and dropped into a solution of potassium permanganate (1:40). The chips immediately commence to decompose the solution and manganese dioxide is deposited upon them, as the following equation shows:—



The chips, after being allowed to blacken thoroughly, are removed, washed, and placed in a solution of sulphurous acid. The liberated hydrogen turned inwards and attacked the colouring matter contained in the wood, producing a superficial bleach.

Commercially, this method is quite workable for the adaption of a cheap and plentiful material, as the actual steepings do not last for more than three hours or so, although better results would be obtained by spreading the two stages over a couple of days. More rapid changes occur if the permanganate be slightly acidulated; this process is discussed *ut infra*.

The neutral-solution method is productive of an excellent whiteness, far superseding the grade of the average white pine so largely in use, while combustibility does not depreciate in the least. On the contrary, it is improved by the part-extraction of the aromatic substances contained therein, figures based upon calorific values having been obtained.

The estimate is based upon recent observations by Datta and Bosu, expanded by the present writer. The *gangwa* commenced to rot after 3 days, and repigmentation took place. Twenty-four hours is a convenient period.

In the case where the permanganate solution is acidulated with sulphuric acid, no beneficial results can be obtained. If, however, a mixture of sulphuric acid and potassium oxalate be used, satisfactory results are obtained. Hot-chamber drying should be replaced by centrifugal drying in this case, eliminating the tendency of the splints to char.

Here, only one stage is necessary, and the treatment can be performed in an hour. The bleach is not so good, and may be provocative of popular prejudice, but the process is cheap and in no way impairs combustibility. It is certainly a debatable point if the cheapness of the *gangwa* wood, plus cost of transport, plus cost of treatment, would compare with the prices paid for the best white pine; but if manufacturers contemplate the experiment, enormous supplies of the wood are available in tropical and sub-tropical localities.

J.M.

## BOOKS RECEIVED.

*Canada To-day*, Edited by ROBERT J. ARNOTT. Pp. 204. 1923. The Canada Newspaper Co., Ltd., 110, St. Martin's Lane, W.C.2. 2s. 6d.

*The Manufacture of Hydrochloric Acid and Saltcake*, by ALEXANDER CHARLES CUMMING, O.B.E., D.Sc., F.I.C. Pp. XV. + 423. Vol. V. 1923. Messrs. Gurney & Jackson, 33, Paternoster Row, E.C.4. 31s. 6d. net.

*Raw Materials for the Manufacture of Sulphuric Acid and the Manufacture of Sulphur Dioxide*, by WILFRID WYLD. Pp. XIII. + 558. Vol. I. 1923. Messrs. Gurney & Jackson, 33, Paternoster Row, E.C.4. 36s. net.

## PUBLICATIONS RECEIVED.

The British Association for the Advancement of Science has just issued as a reprint entitled *The Nitrogen Industry*, a report of the discussion in the Chemical Section of the British Association at the Hull meeting last year.

The discussion was opened by Dr. J. A. Harker, F.R.S., who gave an account of the post-war progress in the Fixation of Nitrogen in England and Abroad.

Mr. J. H. West contributed a paper entitled: *Raw Materials for Synthetic Ammonia: The Manufacture of Hydrogen and Nitrogen*.

Mr. C. J. Goodwin gave a paper on *The Häusser Process of Nitrogen Fixation*, and Dr. E. B. Maxted one entitled *Some Aspects of the Relation between Water Power and Nitrogen Fixation*.

The reprint, price 9d., is published by the Association at Burlington House, W.1.

The Department of Overseas Trade has just issued a report on the *Economic and Financial Conditions in Switzerland, Dec., 1922*, by MR. E. C. D. RAWLINS, Commercial Secretary to H.M. Legation, Berne; pp. 77. Price 2s. 6d.

This report is a valuable resumé of the finance, legislation, trade industries, transport and social matters during the year.



THIS list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

## Latest Patent Applications.

- 9900—Elektrizitätswerk Louza.—Process for preparation of urea salts from cyanamide. April 11.  
 10133—Franck, W.—Manufacture of sulphuric acid. April 13.  
 9779—Thermal Industrial & Chemical (T.I.C.) Research Co., Ltd.—Dehydration and distillation of tar or oils. April 10.  
 10003—Tyrer, D.—Manufacture of phenol and phenolic bodies. April 12.

## Abstract Published this Week.

193722—Synthetic Tanning Agents.—Moeller, W., 20, Billhorner Canalstrasse, Hamburg, Germany.

Coal-tar oils of high boiling point or the hydrocarbons contained therein are subjected to treatment with finely divided sulphur, and the products sulphonated with ordinary or fuming sulphuric acid; the soluble sulphonated products are tanning agents, but may also be used for the same purposes as the non-sulphonated products, for example, as impregnating agents or lubricants. In an example, an anthracene oil of boiling point above 200° C. is heated with powdered sulphur at 100-150° C., and air blown through to remove sulphuretted hydrogen; sulphuric acid is then added and heating continued until the product is soluble in water; after dilution, neutralisation with alkalis, alkaline earths, or oxides or hydroxides of the light metals, the sulphates may be removed by filtration or crystallisation and the remaining solution used directly for tanning. Messrs. Rayner & Co. will obtain printed copies of the published Specification, and forward on post free for the price of 1s. 6d. each.

## PAMPHLETS.

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# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3291.

## BRITISH EMPIRE EXHIBITION.

### SCIENCE AND SCIENTIFIC INSTRUMENTS.

Special efforts are being made by the British Empire Exhibition authorities to have all branches of science adequately represented at Wembley next year, not only in the organised exhibits, but by means of conferences and discussions on scientific subjects. The main objects of the Exhibition are to demonstrate the great resources of the British Empire in raw materials and the capacity and skill of our manufacturers in producing the highest class of goods in every branch of industry. The Exhibition will also show the high position we have attained in music, literature, painting and the arts. Husbandry, the cultivation of gardens, and all the amenities of life will be illustrated. There will be lectures, conferences and cinemas dealing with all phases of our national life.

An impression got abroad at one time that the Exhibition would be visited mainly by millions of people interested in sport and amusements. It is important that this impression should be corrected, and that the public should realise that the outstanding feature of the Exhibition will be its educational purpose in relation to science, art, commerce and industry. Scientific instruments, for instance, will form a notable feature of the Exhibition. It is hoped to include representative surgical, optical, meteorological and photographic appliances.

The latest inventions and the most up-to-date tools of the workshops of science will be brought, by means of this Exhibition, to the notice of a wider public, and new opportunities will be created for the development of trade in those industries.

### THE DECOMPOSITION OF THE AMINOBENZOIC ACIDS BY BOILING WATER.

By L. McMASTER AND R. I. SHRINER.

(Contribution from the Chemical Laboratory of Washington University.)

The decomposition of anthranilic acid, when heated above its melting point, into carbon dioxide and aniline is well known.

Fritzsche<sup>1</sup> identified the gas evolved as carbon dioxide, and Liebig<sup>2</sup> showed that the oily distillate obtained was aniline. Powlewski<sup>3</sup> studied this decomposition and found it to be complete when the acid was heated for 1 hour at 205-210°.

The *m*-aminobenzoic acid yields carbon dioxide, aniline and ammonia on treatment with caustic potash<sup>4</sup>, and the *p*-aminobenzoic acid gives aniline and carbon dioxide when treated with conc. hydrochloric acid.<sup>5</sup> However, no mention is made of the effect of heating aqueous solutions of these acids.

The object of this investigation was to study not only the decomposition of the aminobenzoic acids by boiling water but also to determine the rate of decomposition and the volatility of the acids with steam.

#### EXPERIMENTAL PART.

*Products of Decomposition.* — The presence or absence of aniline and carbon dioxide as products of the decomposition was ascertained by boiling 5g. samples of the pure acids<sup>6</sup> with water under a short reflux condenser for 3 hours, the gases evolved being led into a tube of lime-water protected by a tube of soda lime. The solutions were then neutralised with sodium hydroxide, extracted with ether, and the ether extracts tested for aniline. It was found that the *ortho* and *para* acids gave aniline and carbon dioxide while the *meta* acid did not.

*Rate of Decomposition.* — Weighed samples of the acids were placed in Erlenmeyer flasks and distilled water was added. The flasks were heated just to boiling over the Bunsen flame, and then transferred to an electric hot plate, where gentle boiling was maintained for the desired length of time. During this period the carbon dioxide and aniline escaped from the flasks along with the steam. The quantity of solution was kept constant by the frequent addition of hot water during the boiling period. The flasks were then removed from the hot plate and the undecomposed acid deter-

<sup>1</sup> Fritzsche, *Ann.*, 1841, XXXIX., 86.

<sup>2</sup> Liebig, *ibid.*, 1841, XXXIX., 94.

<sup>3</sup> Powlewski, *Ber.*, 1904, XXXVII., 592.

<sup>4</sup> Beilstein, "Handbuch der Organischen Chemie," Voss, 1896, II., 1,256.

<sup>5</sup> Weith, *Ber.*, 1879, I., 105.

<sup>6</sup> We wish to thank the Monsanto Chemical Works of St. Louis for the anthranilic acid which was prepared and purified by them for us.

mined by titration with standard sodium hydroxide, using phenolphthalein as indicator. The amount of acid decomposed was obtained by subtracting this value from the weight of the sample. Since the amount obtained by this method would also include the acid volatilised with the steam, a correction was made in order to obtain the true decomposition. The average rate of evaporation of water from the flasks, was found to be 100 cc. per hour; so for each hour of boiling the amount of acid per 100 cc. of

water, as determined by the distillation with steam, was subtracted from the total weight of the acid lost.

The steam distillations were carried out in the usual manner using a Claisen flask. The weight of the acid per 100 cc. of distillate was determined by titration with standard alkali. It was found that 100 cc. of the distillate contained 0.016 g. of the *ortho* acid and 0.0056 g. of the *para* acid. The *meta* acid is not volatile with steam.

The following data were obtained:—

TABLE I.  
Anthranilic Acid.

Boiling time Hours	2 g. in 150 cc. water			K	3 g. in 200 cc. water			
	Acid decomp. G.	Acid decomp. Apparent %	Acid decomp. True %		Acid decomp. G.	Acid decomp. Apparent %	Acid decomp. True %	K
1	0.0672	3.36	2.56	0.027	0.0921	3.07	2.54	0.028
2	0.1429	7.15	5.55	0.029	0.1857	6.19	5.13	0.028
3	0.1870	9.35	6.95	0.025	0.3132	10.44	8.84	0.031
4	0.3072	15.36	11.66	0.031	0.4446	14.82	12.69	0.033
5	0.3422	17.11	13.11	0.027	0.5592	18.64	15.97	0.033
6	0.3768	18.84	14.04	0.025	0.6006	20.02	16.82	0.030
7	0.4052	20.26	15.46	0.025	0.6948	23.16	19.43	0.028

TABLE II.  
*Para*-Aminobenzoic Acid.

Boiling time Hours	2 g. in 200 cc. water.			
	Acid decomp. G.	Acid decomp. Apparent %	Acid decomp. True %	K
1	0.0370	1.85	1.57	0.015
2	0.0640	3.20	2.64	0.014
3	0.0852	4.26	3.52	0.013
4	0.1326	6.63	5.51	0.014
5	0.1754	8.77	7.37	0.015
6	0.2025	10.13	9.55	0.017

#### DISCUSSION.

By substituting the decomposition values in the expression for a unimolecular re-

$$\text{action, } K = \frac{1}{0.4343 t} \log \frac{a}{a-x}, \text{ where } a \text{ is}$$

the initial concentration,  $x$  the amount of acid decomposed, and  $t$  the time in hours, the values for the velocity constants were obtained.

In the case of anthranilic acid the values of  $K$  for the initial concentration of 3 g. are greater than in the case of the 2g. sample, apparently indicating an increase in decomposition with increasing size of sample. However, the increase is comparatively

small and is due partly to the fact that the correction for volatility with steam and the error due to mechanical losses during boiling form a smaller percentage of the acid in the case of the 3g. sample than in the case of the 2g. sample.

It is interesting to note that only the *o*- and *p*-aminobenzoic acids decompose into aniline and carbon dioxide and that the *para* acid decomposes only half as fast as does the *ortho*. A possible explanation of these facts may be due to the formation of the inner salt and the subsequent decomposition of this salt.

The *para* acid also forms this inner salt but to a much less extent than anthranilic acid, while the *m*-aminobenzoic acid does not form such a salt at all, and hence does not give aniline and carbon dioxide.

#### SUMMARY.

1. The anthranilic acid and *p*-aminobenzoic acid are decomposed by boiling water into aniline and carbon dioxide, but the *m*-aminobenzoic acid is not.

2. Both anthranilic acid and *p*-aminobenzoic acid are slightly volatile with steam, while *m*-aminobenzoic acid is not.

3. The rate of these decompositions has been studied and the para acid found to be monomolecular. The *para* acid decomposes half as fast as does the *ortho*.

St. Louis, Missouri.

[Reprinted from the *Journal of the American Chemical Society*, Vol. XLV., No. 3. March, 1923.]

### ARRESTING DECAY IN BUILDING STONES.

The question of the deterioration of stonework in buildings is a matter of general economic importance. But in the cases of our historic buildings and ancient monuments prevention of the serious decay and gradual demolition of tooled surfaces and main structures constitutes a special problem which has engaged attention of many investigators for a considerable time without, however, finding any generally satisfactory solution.

### IS THERE AN ELEMENT OF ZERO ATOMIC NUMBER?

By F. H. LORING.

The subject of atomic numbers is of great interest, and the existence of an element, if it may be so called, of zero number may be considered in this connection. To discuss this possibility one must have some basis for the argument.

#### SCHEME.

Act. Elmts. preceding He = 2  
 Ne = 2 + 7 = 9.  
 Ar = 9 + 7 = 16.  
 Kr = 16 + 17 = 33.  
 Xe = 33 + 17 = 50.  
 Rn\* = 50 + 31 = 81.

At. No. He = 2.    2 - 2 = 0.  
 Ne = 10.    10 - 9 = 1.  
 Ar = 18.    18 - 16 = 2.  
 Kr = 36.    36 - 33 = 3.  
 Xe = 54.    54 - 50 = 4.  
 Rn\* = 86.    86 - 81 = 5.

Abbreviations: Act = active. Elmts = elements. At. No. = atomic number.

\* also Tn and An (Emanations) which occupy the same atomic-number place.

The term *element* represents some places or lacunæ which may never be properly filled; but this observation does not apply to the elements below scandium according to the writer's studies (this *Journal*, Vol. CXXV., Nov. 24, 1922, p. 309).

Considering, therefore, the existence of an element preceding hydrogen, it would find a place in many periodic schemes; for example, the one devised by the writer (Wedge

The investigation involved is very complex, and needs to be approached from different angles with the help of wide scientific knowledge.

Accordingly, it has been decided to set up under the Department of Scientific and Industrial Research a special committee of the Building Research Board to report on the best methods by which decay in building stones, especially in ancient structures, may be prevented or arrested.

The Chairman of the Committee will be Sir Aston Webb, K.C.V.O., P.R.A., and the other members will be:—Mr. R. J. Allison, C.B.E., F.R.I.B.A., Professor C. H. Desch, F.R.S., Mr. A. W. Heasman, O.B.E., Mr. J. A. Howe, O.B.E., Sir Herbert Jackson, K.B.E., F.R.S., Dr. Alexander Scott, F.R.S., and Mr. H. O. Weller, M.I.C.E., Hon. A.R.I.B.A.

All communications should be addressed to the Secretary, Department of Scientific and Industrial Research, 16, Old Queen Street, S.W.1.

The following scheme, in the writer's opinion, is suggestive, and while the figured values follow in general of necessity when using Rydberg's numbers, it shows that an *initial* element of zero atomic number could be introduced so as to give a series 0, 1, 2, 3, 4, 5, as shown, completed to its origin.

type) and published in this *Journal*, Vol. CXXV., p. 386. In this case the series 2, 6, 10, 14 will be completed to its origin by introducing this hypothetical member.

In Bohr's recently-published book, *Theory of Spectra and Atomic Constitution*, page 70, a pyramid type of periodic table is shown which appears to be a development of one due to T. Bayley (1882), reproduced in Mellor's *Inorganic Chemistry*, page 810. Bohr

says: "Compared with usual representations of the periodic system, this method, proposed more than twenty years ago by Julius Thomsen, of indicating the periodic variations in the properties of the elements, is more suited for comparison with theories of atomic constitution." In this type of table the element in question could stand at the apex of the pyramid. Whether the table is a "wedge" or a "pyramid" seems to make no difference, but in the former type a numerical rule may be used as an argument in favour of an element preceding hydrogen, that is to say the displacements occasioned by the wedge arrangement lends itself to this treatment. It may be mentioned in this connection, that the object of the Wedge scheme was to correlate the chemical properties of the elements whilst giving the expansions obtained in the pyramid type of table, particularly on account of the rare-earth elements.

Now a certain peculiarity arises from the introduction of a new member at the beginning of the series. In the writer's table (*loc. cit.*, p. 387) this element would fall into the zero group, yet it could not be inactive according to the above rule. Furthermore, an element before hydrogen of atomic weight 1.008 would presumably have to be a fraction. One must proceed cautiously in advancing new ideas, and it can probably be shown that there are just as many arguments for as against the existence of such an element; and, therefore, no probable decision can be arrived at. The subject is, however, a very interesting one, and some further views will be given.

#### NOTES.

The above expression, "Rydberg numbers," refers to the atomic numbers of the inert gases which may be calculated by the well known equation due to Rydberg. The expression, "pyramid table," is not to be taken in the solid-figure sense. It merely means that the table, as drawn, is suggestive of a pyramid, but perhaps a better name could be found. It is convenient to have names for the purpose of identification though they may not be scrupulously accurate when applied to more or less elastic schemes such as periodic tables.

London, S.W.4.

May 12, 1923.

#### PRESERVATION AND USE OF ARTICLES MADE OF RUBBER.

By A. PFESTORF.

When not in actual use, rubber goods should be well wrapped in paper to hinder the access of air and light. They should be kept in a cool place, preferably at a temperature of 10-12° C. Sunlight has a deleterious effect on rubber.

In order to attach rubber tubing to glass or metal, it is usual to damp the inside of the rubber with water or glycerine. Both these methods possess disadvantages, since, in time, the rubber adheres so firmly to the glass or metal, and can only be removed by cutting. This difficulty is overcome if a paste made of a mixture of glycerine with one-third of its weight of talc is used. In this case, when the glycerine is absorbed the talc remains and continues to function as a lubricant.

The exterior diameter of the glass or metal tube should not be much larger than the interior diameter of the rubber.

When used with a metal clip, only rubber tubing of good quality should be used, since this is less likely to adhere by its inner walls when these are pressed in contact for some time. The walls of such rubber should also be thick, so that it may remain supple for a considerable time.—(From *Chemiker Zeitung*, 1923, XLVII., 72.)

#### BRITISH INDUSTRY AND THE EUROPEAN SITUATION.

Sir Eric Geddes delivered a speech on the industrial situation at the seventy-fifth annual meeting of the Association of Trade Protection Societies of the United Kingdom, at the Hotel Cecil, on Thursday, May 10.

Sir Eric reviewed the position of British industry at the present time, and stressed the difficulties of providing work for the large body of unemployed in the face of the collapse of the European markets.

Special emphasis was laid upon the very adverse effects on U.K. trade by the continued occupation of the Ruhr.

## PROCEEDINGS AND NOTICES OF SOCIETIES.

## THE ROYAL SOCIETY.

THURSDAY, MAY 10.

Papers read:—

A. FOWLER, F.R.S. *The Series Spectrum of Trebly-ionised Silicon (Si IV).*

Numerous new lines of silicon have been observed and have been classified in four groups, in extension of the groupings made by Lockyer in connection with stellar spectra. The four groups represent successive stages of ionisation, and have been designated Si I, Si II, Si III, and Si IV. The spectra consist alternately of triplets and doublets, and the series constant has successive values N, 4N, 9N, and 16N.

The present paper deals with the series of Si IV, for which the new data have fully established 16N as the series constant. The spectrum is similar to that of neutral sodium, Na I, but the main series which correspond with the familiar series of Na I are in the extreme ultra-violet, while the second series, which partially fall within the ordinary range of observation, correspond with series which occur in the infra-red in Na I.

Including Paschen's recent work on Al III, and the author's previous work on Mg II, which also have spectra similar to that of Na I, data are thus available for the comparison of the spectra given by four similarly constituted atoms, which differ mainly in the charge of the nucleus. The doublet separations and the series terms show greater regularity than those for elements of the same chemical group.

The highest limit of the Si IV system is 364,117, corresponding to an ionisation potential of 40.6 volts.

SIR R. ROBERTSON, F.R.S., and W. E. GARNER. *Calorimetry of High Explosives.*

The object of this investigation was to determine the quantities of heat and volume of gases produced when high explosives are detonated under standard conditions of confinement and compression, in order to obtain a measure of energy developed, and to investigate nature and reactions of gases evolved.

A calorimetric bomb was devised in which high explosives could be brought to

true detonation under comparable conditions as regards density of loading and confinement, without using a large quantity of explosive. The methods of initiating detonation of the explosive, of determining its heat value, and of measuring gases evolved, are described.

Results are given for some high explosives; and in the case of an explosive balanced in respect to total combustion, where it is possible to calculate values for heat of detonation and volume of gases, the results are shown to be in agreement with these.

The influence of the higher heat of formation of phenol with respect to toluene is shown to be reflected in the similar values for heat of detonation of trinitrophenol and of trinitrotoluene, although the latter has much less oxygen for its combustion.

The paper discusses causes which influence the nature of the products, and the effect of conditions under which detonation is carried out on heat generated, and gaseous reactions involved, chiefly with regard to liberated carbon. The results afforded by imperfect detonation are also quoted.

H. S. HELE-SHAW, F.R.S. *Stream-Line Filter.*

The author points out that in recent experiments he had found very thin films of coloured liquid, or liquid containing matter in very fine suspension, either lose their colour in the one case, or become deprived of their suspended matter in the other, on entering such thin films.

The paper describes a new form of filter, in which sheets of paper made impervious to the fluid containing the suspended matter are arranged in a pack. By perforating the pack with a large number of holes it is possible to get the equivalent of a number of sources and sinks. This was obtained by using high pressures, so as to force the matter from one row of holes, acting as sources between the interstices of the paper, to another row of holes, each hole in the latter acting as a sink.

The use of such a filter enables what would otherwise be a very slow rate of filtration to be made sufficiently rapid for actual use, and the paper gives a description of a laboratory filter constructed on this principle, in which the colouring matter of various dyes, from what were apparently complete solutions, has been removed, while substances like peat water have been rendered clear and colourless.

F. W. ASTON, F.R.S. *A Critical Search for a Heavier Constituent of the Atmosphere by means of the Mass-spectrograph.*

A critical search for a gaseous inert element, heavier than xenon, is described, in which the residues absorbed in charcoal from over 400 tons of air are dealt with.

The final analysis is made by means of the mass-spectrograph. The result is negative and indicates that such an element certainly does not exist to the extent of 1 part in  $10^{15}$  of air, and probably not to the extent of 1 part in  $2 \times 10^{16}$  parts of air by volume.

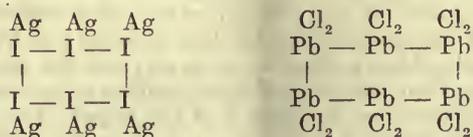
Faint bands observed in the region corresponding to masses 150 and 260 are described and their origin discussed. The first of these is shown to be due to a complex molecule of mercury with a multiple charge, but no conclusion is reached in the case of the other.

The results of the experiments are not in accordance with the presence of molecular krypton and xenon in the air, recently suggested.

Papers read in title only:—

H. E. ARMSTRONG, F.R.S. *Electrolytic Conduction: Sequel to an Attempt (1886) to Apply a Theory of Residual Affinity.*

Referring to the distinction which he drew in 1886 between simple and composite electrolytes—the former being electrolytes *per se*, the latter solutions of “salts”—the author calls attention to the diverse behaviour of the silver and lead haloids on electrolysis; the current being carried, as it were, by the metallic ion of the silver and by the halogen of the lead compound. The conclusion is drawn that the salts of the two metals differ in structure—perhaps thus



The assumption is made that the primarily active unit is the fundamental molecule, and that the circuit is formed by these molecules being coupled with the electrode face and with the complex molecules.

A similar interpretation is applied to aqueous solutions.

H. E. ARMSTRONG, F.R.S. *The Origin of Osmotic Effects. IV.—Hydro-dynamic Change in Aqueous Solutions.*

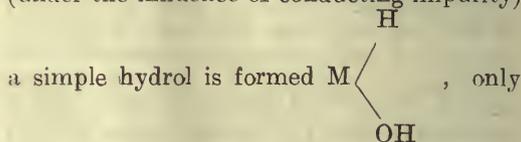
The conclusions arrived at are summarised in the following propositions:—

1. “Water” is a complex saturated with the gas *Hydrone*,  $\text{OH}_2$ . Primarily hydrone is the sole potentially “active” constituent, but it becomes actually active only under conditions which suffice to determine electrolytic change.

2. The vapour pressure of water, or of a solution, is the measure of the proportion of free hydrone molecules present in the liquid.

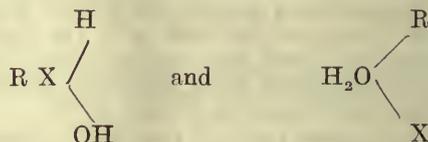
3. Although the vapour pressure is lowered in presence of any solute, the solution acquires attractive properties. The internal activity is increased whilst external activity is diminished.

4. The effect produced may be ascribed to an interaction of molecules of the solute and those of hydrone. From non-electrolytes (under the influence of conducting impurity)

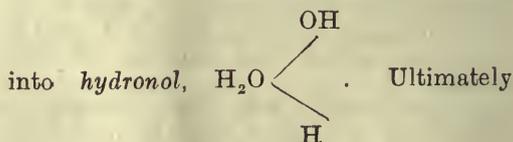
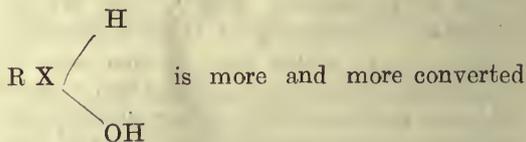


a single molecule of hydrone being “distributed” upon the molecule of the solute, whatever its magnitude.

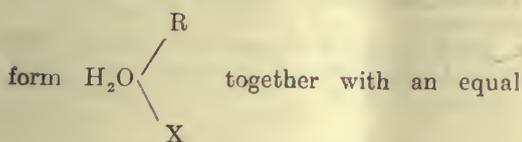
5. In the case of potential electrolytes, a reciprocal interchange of radicles of salt and hydrone is to be postulated. Not only is the solute hydrolated, but it is distributed upon hydrone, the salt  $\text{X/R}'$  giving rise initially to the reciprocal systems



6. As the concentration is lowered, under the influence of hydrone, the complex



the solution contains the solute only in the



number of molecules of hydronol.

7. The "distributed" reciprocal complexes, including hydronol, are the electro-chemical agents in a solution. The negative radicle in such complexes has greater residual affinity than it has in the original simple molecules.

8. The osmotic pressure manifest in an aqueous solution is the pressure exercised by molecules of hydronol acting as though they were present in the gaseous state. In short, osmotic pressure developed within an aqueous solution, whatever the solute, has origin in one and the same cause, and is properly spoken of as *hydrono-dynamic*—if the word be permissible: indeed, this term may be used as expressive of the general activity of water, *electro-chemical and osmotic*.

R. W. WOOD, FOR. MEM. R.S., and A. ELLETT. *On the Influence of Magnetic Fields on the Polarisation of Resonance Radiation*.

It is shown that in the case of the resonance radiation of mercury and sodium vapour strong polarisation of the light can be produced by weak magnetic fields properly orientated, and the polarisation of the light normally present can be destroyed by a magnetic field in a certain orientation. The field strength necessary for the destruction of the mercury vapour polarisation is less than one Gauss.

W. G. PALMER. *A Study of the Oxidation of Copper and the Reduction of Copper Oxide by a New Method*. Communicated by Sir William Pope, F.R.S.

A film of copper about 1/1000 mm. thick is prepared by chemical means on a china-clay rod, which is then clamped in a circuit carrying a small current at constant E.M.F. The film is oxidised at temperatures 130°-210° C. with gaseous oxygen at various pressures up to 1 atmosphere, and the rate of oxidation determined by measurements of the resistance of the film.

The rate of oxidation is proportional to the second power of the amount of metal in the film, and, for pressures up to 300 mm.,

to the square root of the oxygen pressure. Between 170° and 190° C. the temperature-coefficient of the oxidation appears to be negative owing to the simultaneous oxidation of cuprous oxide first formed, some oxygen in the adsorbed film being thus deviated from the metal.

When hydrogen or carbon monoxide is mixed with the oxygen the rate of oxidation is greatly enhanced after a short initial period, during which the rate of oxidation is only slightly less than with oxygen alone. The rate of reduction of copper oxide by hydrogen and by carbon monoxide was studied by similar means. Both gases are adsorbed on the metal present and reduce adjacent oxide, but with hydrogen the water formed also adheres to the metal.

The rate of reduction in both cases is directly proportional to the amount of metal present, an additional term in the case of hydrogen representing the action of the water.

E. A. FISHER. *Some Moisture Relations of Colloids. II.—Further Observations on the Evaporation of Water from Clay and Wool*. Communicated by Prof. A. Smithells, F.R.S.

The study of the evaporation of water from certain colloid materials described in a former paper has been extended to some other materials, notably to kaolin and a ball clay.

The curvature occurring in the evaporation curves of clay soils, which was formerly attributed to shrinkage, is not found in the curves obtained with ball clay, although this substance also shrinks on drying. The particular type of curvature appears to be found only in the evaporation curves of such materials as soils, which are mixtures of colloidal and non-colloidal substances, and is due to the simultaneous evaporation of imbibitional water held by the colloid and of interstitial water held as water-wedges between the soil grains. The former water evaporates at a practically constant rate, while the latter evaporates at a rapidly diminishing rate, curvature in the evaporation curve resulting.

The bearing of these results on the evaporation of water from wool fabrics is discussed, and it is concluded that the linear rate-curve of wool is not inconsistent with a real shrinkage occurring, although so far such a shrinkage has not been demonstrated.

The work is being continued.

THURSDAY, MAY 17.

Papers read:—

A. E. H. TUTTON, F.R.S. (1) *A Universal Interferometer*. (2) *A Wave-length Torsometer and its Use with the Universal Interferometer*.

PROF. L. N. G. FILON, F.R.S., and F. C. HARRIS. *On the Diphasic Nature of Glass as shown by Photo-elastic Observations*.

PROF. C. E. INGLIS. *Stress Distribution in a Rectangular Plate having two Opposing Edges sheared in opposite Directions*. Communicated by Prof. E. G. Coker, F.R.S.

Papers read in title only:—

PROF. T. H. HAVELOCK, F.R.S. *Studies in Wave Resistance—Influence of the Form of the Water-plane Section of the Ship*.

W. M. H. GREAVES. *On a certain Family of Periodic Solutions of Differential Equations, with an application to the Triode Oscillator*. Communicated by Prof. H. F. Baker, F.R.S.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

The Friday evening discourse on May 18, at 9 o'clock, will be delivered by WILLIAM MORRIS MORDEY, Past Pres. I.E.E., M.-Inst.C.E., M.R.I. The subject is *Recent Studies in Alternating Magnetism* (with experiments).

On Tuesday, May 15, PROF. A. C. SEWARD, Sc.D., F.R.S., gave a lecture on *Arctic Vegetation of Past Ages*.

On Thursday, May 17, PROF. E. G. COKER, D.Sc., F.R.S., M.R.I., delivered a paper on *Engineering Problems solved by Photo-elastic Methods*.

The General Monthly Meeting of the members of the Royal Institution was held on May 7, the Duke of Northumberland, President, in the chair.

Sir J. J. Thomson was elected Honorary Professor of Natural Philosophy, and Sir Ernest Rutherford Professor of Natural Philosophy.

It was announced that the Duke of Northumberland, President, had nominated the following gentlemen as Vice-Presidents for the ensuing year: Dr. Mitchell Bruce, Lord Iveagh, Sir Edward Pollock, Lord Rothschild, Sir Alfred Yarrow, the Rt. Hon. Lord

Justice Younger, Sir James Crichton-Browne, treasurer, and Sir Arthur Keith, secretary.

Dr. P. J. Le Riche and Dr. Liebert were elected members.

#### THE CHEMICAL SOCIETY.

An informal meeting was held on Thursday, May 17, 1923, after the conclusion of the formal business of the Ordinary Scientific Meeting.

#### ROYAL SOCIETY OF ARTS.

On Monday, May 14, the third Howard lecture, entitled *The Development of the Steam Turbine*, was delivered by STANLEY S. COOK, B.A. (CANTAB.), M.I.N.A., M.I.M. (of Parsons Marine Steam Turbine Co.).

On Wednesday, May 16, at the Ordinary Meeting, MR. LEON GASTER, F.J.I., Editor of *The Illuminating Engineer*, read a paper entitled *Industrial Lighting and the Prevention of Accidents*. Sir Malcolm Delevingne, K.C.B., Assistant Under-Secretary of State, Home Office, presided.

#### SOCIETY OF GLASS TECHNOLOGY.

A meeting of the Society was held in the Physical Chemistry Theatre, University College, Gower Street, London, W.C.1, on Wednesday, May 16.

The following papers were received and discussed:—

*On the Refractive Index Changes in Optical Glass occasioned by Chilling and Tempering*, by F. TWYMAN, F.INST.P., and F. SIMEON, B.Sc., F.INST.P.

*Notes on Burettes*, by VERNEY STOTT, B.A., F.INST.P.

*A New Method of Glass Melting*, by A. FERGUSON.

*The Drying out and Warming Up of Tank Furnaces*, by C. SAXTON, A.M.I.E.E.

*Notes on the Design of Pot Arches*, by TH. TEISEN, B.Sc., C.E.

#### WORKS VISIT.

By the courtesy of the Directors, a visit was arranged on the morning of Thursday, May 17, to the new works of Messrs. James Powell & Sons (Whitefriars), Ltd., Wealdstone, Harrow.



## THE OPTICAL SOCIETY.

A meeting was held at the Imperial College, Imperial Institute Road, South Kensington, on Thursday, May 10, when a paper on *Stereoscopy Re-stated*, by DR. J. W. FRENCH, F.INST.P., was read and discussed.

## THE FARADAY SOCIETY.

Papers read on May 14:—

*Some Notes on the Etching Properties of the  $\alpha$  and  $\beta$  Forms of Tri-carbide of Iron*, by FRANK CHARLES THOMPSON, D.MET., B.Sc., and EDWIN WHITEHEAD.

In the course of some work on the etching properties of the carbides in alloy steels it was noticed that a dilute solution of ammonium oxalate, which according to Matwieff stains cementite red, did not produce this effect. In a tungsten steel one of the constituents of which was a carbide which had shown the etching characteristics of cementite, it was found that with the Matwieff reagent a deep reddish coloration was produced.

It was believed that a small amount of tungsten in the carbide might cause the retention of that form which is normally stable only above 200° C. The change commences at 160° C., and is complete about 200° C. At even lower temperatures than 160° there may be some modification of cementite. Further, if a white cast iron, or a high carbon steel is quenched at 280° C. so that the high temperature, or  $\beta$  form, of carbide is retained down to normal temperatures, the electrical resistance undergoes a gradual fall. This means that the cementite in the  $\beta$  form is tempered at room temperatures and slowly reverts to the  $\alpha$  state.

The instability of  $\beta$  cementite has rendered it difficult to obtain sharp differences in etching properties. Further, the differences which are fairly clearly shown immediately after the quenching soon cease and indistinct structures are obtained.

The heatings were effected in an oil bath, and duplicate specimens were quenched from 270° C., and slowly cooled in the oil respectively. In the case of the Swedish white iron a third sample was cooled from 190° C., a temperature at which some, but not all, of the changes have occurred. At each temperature the samples were allowed

to remain for a period of one hour before they were cooled.

It is of interest that the authors have been unable to obtain a suitable etching with ammonium oxalate of cementite in either form. At times a very faint pink coloration was observed, which was insufficiently pronounced to be of value.

It is also remarkable that despite the well-known fact that a hot solution of alkaline sodium picrate will darken carbide of iron, neither the sodium picrate nor the caustic soda will effect this by themselves.

The reagents which darkened cementite are:—

- (1) Alkaline sodium picrate;
- (2) Alkaline sodium benzoate, 6.3 grams benzoic anhydride, 20 grams caustic soda, and 100 cc. water, used hot for 30 minutes.
- (3) Alkaline potassium ferricyanide, Murakami's reagent—4 minutes at 100° C.
- (4) Le Chatelier's reagent, *viz.*, a boiling solution of 10 per cent. lead nitrate with an equal volume of 50 per cent. caustic soda, etches in 5 minutes.
- (5) A boiling solution of alkaline copper potassium cyanide.
- (6) A 10 per cent. solution in water of ammonium molybdate. Etches the carbide in the cold in 18 hours.
- (7) An alkaline solution of ammonium molybdate aided by a small electric current. Etches cementite in a few minutes.

No acid solution will darken cementite, and, with the exception of the ammonium molybdate solution, and that very slowly, no neutral solution was discovered which will do this. None of the reagents possess any marked advantage over the standard alkaline sodium picrate, though some act a little more quickly. Murakami's reagent, aided by a small electric current, is quite useful and possesses potentialities as a means of differentiating between the two forms of carbide.

*An Example of Polymorphism in an Inter-Metallic Compound*, by DAVID STOCKDALE, B.A.

The author has recently determined the liquidus of the copper rich aluminium-copper alloys, using sensitive apparatus for measuring temperatures.

Between 9 and 18 per cent. by weight of aluminium, this liquidus is a smooth curve which is described in a remarkable manner by the equation—

$$T = -x^2 + 25x + 891,$$

where T is temperature in degrees Centi-

grade, and  $x$  is the percentage of aluminium by weight, the origin being ( $T = 0^\circ \text{C.}$ ,  $x = 0$  per cent. aluminium).

Between 18 and 22 per cent. the equation—

$$T = -2.8x^2 + 97.4x + 169$$

agrees closely with observed values.

A compound having the formula  $\text{Cu}_2\text{Al}$  would contain 17.6 per cent. of aluminium. The two equations which describe the experimental results so well would show that the compound  $\text{Cu}_2\text{Al}$  does exist, but that it is unstable above  $1,015^\circ \text{C.}$

If the compound is formed at  $1,015^\circ \text{C.}$  it is to be expected that cooling-curves of alloys between, say, 16 per cent. and 18 per cent., would show thermal arrest points at that temperature, due to the heat of formation of the compound  $\text{Cu}_2\text{Al}$ . Experimentally, this is found to be the case, though, as the evolution of heat is small, the temperatures are difficult to measure with accuracy. The 16.5 per cent. alloy shows a point at  $1,015^\circ \text{C.}$ , the 17 per cent. at  $1,016^\circ \text{C.}$ , and the 17.5 per cent. at  $1,017^\circ \text{C.}$  The 18 per cent. also probably shows an evolution of heat, but it is merged in the large quantity of heat evolved as the alloy first freezes.

Further evidence for the existence of  $\text{Cu}_2\text{Al}$  lies in the fact that the nearer the composition approximates to 17.6 per cent. of aluminium the harder is the alloy to etch. A body of the above composition is extremely resistant to acids.

*The Elasticity of Organogels of Cellulose Acetate*, by ERNEST WALTER JOHN MARDLES, M.Sc. (LOND.), F.I.C.

The determination of the elasticity of a gel is complicated by the persistence of strain after removal of stress, so that the elasticity is perfect only for small stresses applied for a short time. The phenomenon of plastic strain has been studied with different materials, and the general conclusions are applicable to the elastic properties of jellies. Various workers have distinguished between (a) the instantaneous elastic deformation which disappears simultaneously with the suppression of the stress (primary or elastic strain), (b) the reversible deformation which is a function of time (secondary strain, subpermanent deformation, or reactivity), and (c) viscous or plastic flow, which is irreversible with time and produced at constant rate.

Hatschek observed that optical anisotropy, caused by straining prisms of gelatine gel (10 per cent.), did not disappear

with the removal of stress. The experiments, repeated with gels of cellulose acetate in benzyl alcohol, gave similar results, the period of observation extending over several weeks.

The materials used were the same as those employed for the other experiments on the reversible sol-gel transition. Young's modulus was measured by observing the extension of rods or strips on loading, by means of a travelling microscope. The specimens were contained in a constant temperature and humidity chamber, whilst under examination, since the modulus is considerably affected by temperature changes, also by humidity changes on account of the hygroscopic nature of the cellulose derivative. The relative modulus of rigidity of the organogels was determined by a method similar to that used by Rankine, *viz.*, allowing about 100 grams of the sol to set between two coaxial cylinders, the diameter of the outer being 4.5 cm. whilst the diameter of the inner was varied at will, according to the degree of rigidity of the gel under examination. The outer cylinder was fixed and a known weight acting over a light pulley tended to rotate the inner. The angles of twist produced by small loads were observed by means of a scale fixed at a distance of about 50 cm., a small correction being applied for the friction of the pulley.

The relation between the modulus of elasticity and concentration for the organogels of cellulose acetate is not expressed by any simple formula. The expression  $E = kC^n$  represents the relation approximately at higher concentrations over limited ranges. The value of  $n$  decreases with fall in temperature. The relation between  $\log E$  and temperature is approximately rectilinear over the range of temperature examined. The physical significance of these relations is discussed.

Addition of substances to the gel mainly affects the modulus in proportion to the change in the number of particles which aggregate.

The changes, with time, in the modulus of rigidity of the gels, associated with the reversible sol to gel transition, have been studied. The significance of the shape of the curves relating elasticity and time, has been discussed.

*The Vapour Pressures of Concentrated Cane Sugar Solutions*, by EDGAR PHILIP PERMAN and HORACE LEONARD SAUNDERS.

Many measurements have been made of the vapour pressures of dilute solutions, but

comparatively little has been done on those of higher concentrations except at low temperatures.

The experiments in this investigation have been confined to cane sugar, and observations have been made with concentrations from 10 per cent. to saturation; in a few cases it has been possible to use a solution which was supersaturated. The measurement of the vapour pressure is a direct one, the actual pressure of the vapour being balanced against a column of mercury. It was found that Babo's Law held for sugar solutions.

*Some Experiments on the Hardness and Spontaneous Annealing of Lead*, by A. L. NORBURY, M.Sc.

*Part I.*—Description of an adaptation used for making Low Load Brinell Impressions with a Lever Tensile Machine.

*Part II.*—Brinell Hardness Tests on Lead using various Loads maintained or Various Lengths of time. Results interpreted according to Meyer's Formula:  $L = ad^n$

*Part III.*—Effect of Cold-Hammering on the Hardness of Lead. Results showing (a) Increase in Hardness, and (b) Spontaneous Annealing.

I.—Brinell hardness tests on lead showed that the time during which the load was maintained was an important variable. Differences of seconds had appreciable effects on the diameters of the Brinell impressions produced. To make tests on lead it was necessary to use a machine in which the load could be applied and removed almost instantaneously. Moreover, owing to the fact that lead is such a soft metal, only loads up to about 300 kg. can be used with a 10 mm. ball.

The lever tensile machine used was an adapted 10 ton Buckton, and it fulfilled the requirements.

II.—The specimens of lead tested were cut from an ingot of Cookson's chemically pure lead (99.99 per cent. Pb.).

The surfaces on which the Brinell tests were made were filed and emery papered down to O emery, and were then annealed at 100° for 1 hour to remove any surface hardening effects.

The time of maintaining the load is a very important variable which must be accurately determined when measuring the Brinell hardness of lead. It is also obviously necessary to make each impression on a fresh surface—as distinct from the method of making concentric impressions which is permissible in the case of harder metals.

III.—The time taken to reduce a lead specimen to a given thickness varied between about 1 and 8 seconds. The specimen was then rapidly transferred to the testing machine, and the first Brinell impression made 20 seconds after completion of hammering. Further impressions were made at intervals. It was difficult to control the conditions of hammering very exactly and there are certain obvious variables.

Lead is hardened by cold-work, and it was shown that, within certain limits, the greater the amount of cold-work the greater the hardening. It is spontaneously annealed at room temperature (16° to 18°). The rate of annealing increases with the amount of deformation, and this introduces an interesting result in that lead which has been very severely hammered shows no increase in hardness. The severe deformation in this latter case has caused such rapid annealing that the lead is dead soft 20 seconds after hammering.

#### THE GEOLOGICAL SOCIETY.

At the meeting on May 2, Prof. A. C. Seward, Sc.D., F.R.S., President, in the chair, Prof. JOHN JOLY, D.Sc., F.R.S., delivered a lecture on *The Bearing of some Recent Advances in Physical Science on Geology*.

After referring to the discovery by the present Lord Rayleigh of the general distribution of radioactive materials and to the earlier but more recently developed discovery of isostasy, the lecturer observed that, assuming that the dense layer upon which, according to the theory of isostasy, the continents float, is composed of basalt possessing the average radioactivity of basalts, it may be calculated that if this substratum is now solid (as appears from both tidal and seismological evidence), it will have acquired sufficient radioactive heat to become fluid in about 30 million years.

The change of density then occurring will cause a downward motion of the continents relative to the ocean, and transgressional seas will result. After a long period, during which the liquid magma (under tidal forces) circulates from beneath the continents (which, owing to their own radioactivity, act as an adiabatic covering) to suboceanic regions, the accumulated heat is given up to the ocean. Re-solidification of the magma ensues, and the restoration of

the former higher density causes the continents to rise relatively to the oceans, and brings about the retreat of transgressional seas. In this manner, the complete cycle of a revolution finds explanation.

Mountain-building forces arising during the climax of revolution originate from two sources:—(a) the effects of the horizontal tide-generating force and of precessional force which, although probably considerable, have not yet been evaluated; (b) the effects of the changing area of the ocean-floor attending the expansion and contraction of the basaltic layer, whereby the oceanic area becomes alternately increased and diminished. Upon shrinkage the enlarged ocean-floor bears against the continents. Hence "the highest mountains confront the widest oceans."

Mountain-building is due much more to vertical than to horizontal forces. The mountains are not pushed up by lateral forces: these forces act upon the subsidising geosyncline to produce deformation of the semi-plastic materials. The mountains are elevated long after by the isostatic forces, the energy being traceable to the stored radioactive heat of prior ages.

Inter-revolutionary events consist of "preparatory" disturbances, due to local increase of liquefaction of the magma; also of "sequential" disturbances, due to relief of strain accumulated during revolution, and to the restoration of isostatic equilibrium.

The conditions now prevailing beneath the continents preclude the establishment of a steady state (that is, of thermal equilibrium) and in the past always must have done so.

The cyclical events outlined in the theory here adduced appear to be inevitable as a consequence of radioactivity and isostasy. Cyclical disturbances alone can explain the past history of the Earth's surface.

At the meeting held on Wednesday, May 16, the following communications were read:—

*The Upper Ordovician Rocks of the South-Western Berwyn Hills*, by W. B. R. KING, O.B.E., M.A., F.G.S.

*The Geology of the District around Corris and Aberllefenni (Merioneth)*, by PROF. W. J. PUGH, O.B.E., B.A., F.G.S.

A lecture on the Geology of Novaya Zemlya was delivered by Dr. Olaf Holte-dahl, on Thursday, May 17, in the Geological Department, Imperial College of Science and Technology, Prince Consort Road, S.W.7. Prof. W. W. Watts, Sc.D., F.R.S., presided.

## ROYAL AGRICULTURAL SOCIETY OF ENGLAND.

PROCEEDINGS AT MONTHLY COUNCIL, HELD ON WEDNESDAY, MAY 2, LIEUT.-COL. E. W. STANYFORTH (PRESIDENT) IN THE CHAIR.

Among other business, the following reports were presented:—

### *Chemical.*

Mr. Luddington reported that the Consulting Chemist had presented the list of samples analysed by him for members during the past month, and had submitted various matters arising out of his correspondence.

### *Research.*

Mr. Adeane, in the absence of the Duke of Devonshire, reported that statements had been received as to the progress of the following experiments which were being carried on for the Society:—

- (1) Norfolk Agricultural Station (barley and other cereals).
- (2) National Institute of Agricultural Botany (oat trials).
- (3) Mr. Arthur Amos (silage).
- (4) Mr. Thomas Hacking (grassland improvement—Leicestershire).
- (5) Professor Seton (grassland improvement—Yorkshire).

With regard to the republication of the results of past experimental work of the Society, it had been resolved that Dr. Voelcker and Sir John Russel be asked to proceed at once with the collation of the material relating to cereals in the past volumes of the Society's Journal, as well as similar material available at Rothamsted, but that Lord Bledisloe and Mr. Orwin be consulted prior to the publication of the work or its reproduction in the Society's Journal.

It had been finally determined with regard to the yield trials of oats being conducted for the Society by the National Institute of Agricultural Botany that the contribution from the Society was not to exceed £816 for the two years.

Mr. Adeane moved the adoption of this report. As two of the experiments—one on pig feeding by Professor Wood and the other on silage by Mr. Amos—were being carried out at Cambridge, he suggested that if possible arrangements should be made so that members of Council who wished to do so could go to Cambridge after the Council Meeting on August 1. He proposed that

the Council Meeting on that day should be held at 10 o'clock, in order that those who wished to take part in the visit could catch an early train.

Mr. Dampier Whetham said that although he had no official connection with the School of Agriculture, he knew the views of Professor Wood and others concerned at Cambridge, and was able to support very warmly Mr. Adeane's suggestion.

The President asked if it was the wish of the Council, after hearing what Mr. Adeane had said, that they should hold their meeting at 10 o'clock on August 1.

This was agreed.

Other business having been transacted, the Council adjourned until Wednesday, June 6 (Derby Day), at 10 a.m.

#### THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

*Heavy Grade Egyptian Crude Petroleum*, by W. A. GUTHRIE, F.I.C., F.R.S.E., etc.

(Owing to Mr. Guthrie's absence in Egypt, this paper was read by Professor J. S. S. Brame, F.I.C., F.C.S.)

According to Hume, seepages of oil at Zeitia, Gensah and Gebel Tanka, the latter on the coast of West Sinai, led to the Egyptian borings for oil. Important supplies were first obtained at Gensah in 1908, where the petroleum was present in porous dolomitic limestone associated with gypsum, of Miocene age. Subsequently in 1913 borings were commenced at Hurghada. These traversed the typical Miocene succession as developed on the surface in the Zeit Hills—viz., below a thick series of gypsum followed dolomitic limestone or the characteristic Globigerina Marl. Below this stratum is a series of sands and shales (including carbonaceous varieties), in which the main oil is present. A third small oil-field is the Abu Durba, on the west coast of Sinai, where there are indications of the former presence of oil in the Nubian Sandstone. Borings have shown that petroleum is present in gravels of igneous rocks occurring between the outcrop of the Nubian sandstone and the shore. Whether the oil is present in deeper seated strata has still to be shown.

The heavy grade crude petroleum is found at Hurghada (Rargada), 200 miles S.E. of Suez. From the striking of oil in the first well in October, 1914, until the beginning of the present year, 1,201,868 metric tons have been won. The present production averages

3,500 tons per week. A proportion of the production of the field is "wet"—i.e., contains about 30 per cent. of salt water as a very refractory brine emulsion, difficult to de-emulsify.

In 1918 the author carried out experiments confirming that these emulsions were amenable to the electrical dehydrating treatment.

The oil is a mixture of paraffin base and asphaltic base petroleum; it has quite a pleasant smell, despite its sulphur content, and when seen in a thin film is brownish-black in colour, while the calorific value is just under 19,000 B.T.U.s per pound. It contains traces of Vanadium and Nickel. The ultimate analysis is: carbon, 85.15 per cent.; hydrogen, 11.71 per cent.; sulphur, 2.25 per cent.; oxygen and nitrogen (by difference), 0.89 per cent.

Although much study has been expended on chemical examination, this is still incomplete. The only practical method of separating the constituents is fractional distillation, which, at atmospheric pressure, alters the composition of the fractions. In order to obtain fractions having a closer relationship to the original crude oil, distillations were conducted right down to eoke, under a vacuum of 28 inches, using liberal supplies of steam. The final temperature of the vapour was 223° C. In the earlier fractions from these vacuum distillations, very little, if any, bromine was absorbed; in the earlier fractions from an atmospheric distillation 3 to 10 per cent. unsaturated hydrocarbons occur. Moreover, in the later fractions from an atmospheric distillation as much as 40 per cent. of unsaturates have been found, while in the same fractions, from a vacuum distillation, these were from 10 to 20 per cent.

The oil, when distilled in the ordinary way for commercial products, yields 6 to 8 per cent. benzine boiling below 150° C., and 14 to 15 per cent. kerosine, boiling between 150 and 290° C.

The benzine and kerosine fractions can be refined to first-class products. The benzine is not entirely free from sulphur compounds but these are not present in an objectionable form.

The kerosine (specific gravity, 0.820 at 15.5° C.) can be refined to a water white kerosine of high illuminating value, by treatment with 2 per cent. of sulphuric acid, finishing with fuller's earth or florida clay treatment.

The residue is very thick and viscous, becoming semi-solid at temperature slightly below 15.5° C., and having a viscosity at 100° F. in Redwood's No. 1 Viscometer of anything from 5,000 to 7,500 secs. The viscosity cannot be determined at all in the No. 2 Viscometer at 32° F., or even at 60° F. The high viscosity is, of course, due to the asphalt and paraffin wax content, which amounts to 15.25 per cent. of the former, and 10.35 per cent. of the latter. The calorific value of the residue is 18,370 B.T.U.s.

On analysis a typical sample of the still coke gave: Carbon, 96.76 per cent.; sulphur, 2.96 per cent.; ash, 0.28 per cent.

#### "THE PHYSICAL CHEMISTRY OF THE PHOTOGRAPHIC PROCESS."

The Society will hold a general discussion on this subject on Monday, May 28 next, in the Hall of the Institution of Electrical Engineers, Victoria Embankment, W.C.2. Professor W. D. Bancroft, of Cornell University, will open the proceedings at 3 p.m. with an Introductory Address on *The Theory of Photography*. This will be followed by detailed consideration of the subject, subdivided as follows:—

I. "The Physical Chemistry of the Vehicle and of the Emulsion."

II. "Reactions in the Plate during Exposure."

III. "Development and Characteristics of the Developed Plate."

IV. "Adsorption Reactions in Photographic Films."

Each Section will be introduced by a Preliminary Address and followed by general discussion. Among those who will read papers are Dr. T. Slater Price, Dr. F. C. Toy, Mr. Olaf Bloch, Mr. T. Thorne Baker, M. Clerc, Prof. Luther, and Prof. Goldberg. Several communications will be made from Mr. S. E. Sheppard and other members of the staff of the Eastman Kodak Company, and papers are also expected from Dr. Chr. Winther, Dr. Lippo Cramer, and Prof. L. Plotnikov.

Between the afternoon and evening sessions a complimentary dinner will be given at the Hotel Cecil to Prof. Bancroft and the other guests.

Members of the Chemical Society are invited to attend this meeting. Full particulars may be obtained from the Secretary of the Faraday Society, 10, Essex Street, London, W.C.2.

#### GENERAL NOTES.

##### SANITARY INSPECTION OF ARGENTINE AGRICULTURAL EXPORTS.

A recently issued Presidential Decree, which is to come into force in July next, lays down regulations for the sanitary inspection of agricultural products exported from the Argentine Republic.

The Minister of Agriculture is to organise in the ports of Buenos Aires, La Plata, Bahia Blanca, Rosario, in the city of Mendoza (and in other ports when convenient) an inspection service for plants, shoots, tubers, bulbs, seeds and grain, fresh fruits and vegetables destined for export, in order to ascertain their sanitary state, conditions of packing and shipment.

Exporters are required to apply to the Minister of Agriculture, in the prescribed form, for permission to export each consignment.

Detailed instructions respecting the nature of the inspection, analysis, or cleaning necessary for each category or class of produce are specified in the Decree, which provides for the issue of certificates if the goods are recognised as suitable for export.

A copy of the Decree in Spanish may be seen by persons interested on application to the Tariff Section of the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.

##### FOREIGN SAMPLES EXHIBITION AT WALSTALL.

An exhibition of foreign samples and catalogues held at the offices of the Walsall Chamber of Commerce on May 3 and 4 proved one of the most successful displays yet held at that centre.

The samples exhibited, particulars of which appeared in the *Board of Trade Journal* of April 26 (page 501) proved of exceptional interest to the manufacturers of Walsall and district, who expressed their ability to compete with the foreign-made article.

A full attendance was recorded, whilst 124 samples and 150 catalogues were borrowed by firms who desired to consider carefully the question of export of similar goods. The fact that over 40 definite enquiries were received for names of buyers and information respecting export matters indicates that Walsall firms intend to make practical use of the lessons of the exhibition.

## LJUBLJANA TRADE FAIR.

The Department of Overseas Trade is informed that the Third Ljubljana (Laibach) International Trade Fair will be held from September 1 to 10.

There is a market in Jugo-Slavia for automobiles, parts and accessories; metal goods; celluloid products; chemical and pharmaceutical products; electro-technical and other machinery; bicycles and accessories; typewriting machines and ribbois; office equipment; perfumery; optical instruments; sports equipment; watches and clocks; jewellery and fancy goods.

Stand prices vary from 60 to 160 dinars per square metre, according to the position of the stand.

A booklet and specimen application form (in French) may be seen on application to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.—(From the "Board of Trade Journal," May 10.)

## DYESTUFFS (IMPORT REGULATION) ACT.

## APPLICATIONS FOR LICENSES IN APRIL.

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during April has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee.

The total number of applications received during the month was 512, of which 430 were from merchants and dealers. To these should be added the 22 cases outstanding on April 1, making a total for the month of 534. These were dealt with as follows:—

Granted—331 (of which 318 were dealt with within seven days of receipt).

Referred to British makers of similar products—130 (of which 121 were dealt with within seven days of receipt).

Referred to Reparation Supplies available—56 (all dealt with within two days of receipt).

Outstanding on April 30—17.

Of the total number, 534, of applications received, 479, or 90 per cent., were dealt with within four days of receipt.

UNIVERSITY OF LONDON,  
UNIVERSITY COLLEGE.

On Friday, May 11, the Rt. Hon. the Viscount Chelmsford, G.C.S.I., G.C.M.G.,

G.C.I.E., G.B.E., Chairman of the College Committee, unveiled the tablet commemorating the munificent gifts for the new chemistry building made by Sir Ralph Forster, Bt., J.P.

The chemistry laboratories were open to inspection after the ceremony.

## NOTICES OF BOOKS.

*Einführung in die Kolloidchemie*, von PROF. DR. VIKTOR PÖSCHL. Sechste verbesserte Auflage. Pp. 158. Dresden and Leipzig: Verlag von Theodor Steinkopff. 1923. Price 3s. 1d.

The appearance of the sixth edition of this very clearly written *Introduction* shows how widely Prof. Pöschl's little volume is used for the study of Colloid Chemistry. It will certainly continue to fulfil the author's intentions, as expressed in the preface, as a text-book by those who wish to gain a clear conception of the phenomena in this branch of natural science.

His endeavours to establish colloid chemistry as an *exact* science will meet with general approval.

The book constitutes an interesting survey of the subject and gives a clear conception of various colloidal phenomena. It also points to the ways in which a knowledge of these phenomena can be utilised in dealing with other chemical and technical problems.

The advent of this edition is opportune since the elementary study of colloids will be included more and more in science curricula. Prof. Pöschl's book will therefore be found very valuable for students, since it is sound and precise, and will leave a correct impression in the students' mind. V.K.

*Synthetic Inorganic Chemistry*, by ARTHUR A. BLANCHARD, Ph.D., and JOSEPH W. PHELAN, S.B. Third edition, entirely rewritten and greatly enlarged. Pp. XIV. + 321. London: Messrs. Chapman & Hall, Ltd., 11, Henrietta Street, W.C. 1922. Price 15s. net.

The authors of this volume on practical inorganic chemistry rightly commence with an introduction on manipulation and general laboratory processes. Early chapters are devoted to the quantitative aspects of chemistry, solution, and experiments illustrating the theory of Ionisation.

Subsequent chapters give numerous methods of preparations of compounds, grouped according to the Periodic Classification of the elements. The preparations are followed by further illustrative experiments

and each chapter concludes with a set of questions designed to test how far the student has grasped the subject matter.

The volume abounds in explanatory details, and has evidently been revised in accordance with the latest knowledge, although in the case of the appendix on the *Periodic Classification of the Elements according to their Atomic Numbers and the Arrangement of their Electrons*, this seems to have been done rather hurriedly. The outstanding advantages outweigh any minor defects of this nature, which can be remedied in the next edition.

The practical exercises are arranged to follow lecture work. Practically every type of chemical reaction is exemplified in the course outlined. This is done in such a manner as to preclude the operations being conducted in a mechanical manner.

These are among the many good points to be noticed in a perusal of this work.

#### BOOKS RECEIVED.

*The Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes*, by PROF. DR. D. HOLDE. Pp. XIX. + 572. Second Edition. 1922. Messrs. Chapman & Hall, 11, Henrietta Street, Covent Garden, W.C.2. 30s. net.

*Thermodynamics and the Free Energy of Chemical Substances*, by GILBERT NEWTON LEWIS and MERLE RANDALL. Pp. XXIII. + 651. First Edition. 1923. Messrs. McGraw Hill Publishing Co., Ltd., 6 & 8, Bouverie Street, E.C.4. 25s. net.

*Synthetic Inorganic Chemistry*, by ARTHUR A. BLANCHARD, PH.D., and JOSEPH W. PHELAN, S.B. Pp. XIV. + 321. Third Edition. 1922. Messrs. Chapman & Hall, Ltd., 11, Henrietta Street, Strand, W.C.2. 15s. net.

*Practical Chemistry*, by E. J. HOLMYARD, M.A. Pp. XVI. + 264. 1923. Messrs. G. Bell & Sons, Ltd., York House, Portugal Street, W.C. 4s. net.

*The Chemistry of Urea*, by EMIL A. WERNER, M.A., Sc.D., F.I.C. Pp. X. + 212. 1923. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 14s. net.

#### PUBLICATIONS RECEIVED.

The Board of Agriculture and Fisheries has issued a leaflet, No. 246, entitled *Prevention of Damage to Hides, Skins, and Wool*.

Among the most important live stock products, after the meat itself, are the hides

of cattle and the wool and skin of sheep. These are, it is true, bye-products in the sense that the animals are primarily grown for meat and not for their hides or skins, but they are bye-products of very considerable value, and as such deserve more attention at the hands of farmers and others interested in the live-stock industry than they commonly receive.

The value of these bye-products is frequently depreciated by causes which are recognised as injurious in other ways, but which are not usually regarded as necessarily affecting the price which the farmer receives for his stock and produce. The loss in value thus caused is a serious matter.

Leaflet No. 242, "Stripe" Disease of Tomatoes, is abridged from an important article by S. G. Paine and W. F. Bewley in the *Journal of the Ministry of Agriculture*, January, 1920.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 10583—Badische Anilin & Soda-Fabrik.—Production of tanning materials. April 18.
  - 10804—Chemische Fabrik Auf Aktien vorm. E. Schering.—Manufacture of vaccines from bacteria. April 20.
  - 10592—Kuhn, A.—Apparatus for extraction and removal of resin from solution in acid. April 18.
  - 10883—Vogal, H.—Process for manufacture of colloidal sulphur. April 21.
- Specifications Published this Week.*
- 195710—Zahn, E.—Process and apparatus for concentrating liquids.
  - 195753—Soc. of Chemical Industry in Basle.—Manufacture of vat dyestuffs derived from anthraquinone.
  - 195798—West, J. H., Jaques, A., Tully, C. B.—Manufacture of hydrogen or gases rich in hydrogen.

#### Abstract Published this Week.

- 194244—Dyeing cellulose acetate.—British Cellulose & Chemical Manufacturing Co., Ltd., 8, Waterloo Place, London, and Bader, W. Spondon, near Derby.

The partial alkaline saponification of cellulose acetate threads, films, or fabrics, to facilitate dyeing, is carried out by first treating the goods with a hot or cold salt solution, and then saponifying with substantially cold caustic alkali. If desired, a little alkali or alkaline-earth hydroxide may be added to the salt bath, to prime the subsequent saponification. Sodium, calcium, or magnesium chloride are suitable salts for the pretreatment bath. Mixed goods containing cellulose acetate and cellulose threads may be treated by the process.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the price of 1s. 6d. each.



## THE CHEMICAL NEWS,

VOL. CXXVII. No. 3293.

AN EXPLANATION OF THE THEORY  
OF THE ROTATION OF THE ATOMIC  
NUCLEUS.

PART II.

BY HERBERT HENSTOCK.

Before proceeding to apply the theory to specific cases there is one conception of a general nature, which should be realised in order fully to appreciate the workings of the nucleus. Let us consider two neighbouring atoms of a chain, the one positive, the other negative. The nucleus of the negative atom is using a considerable amount of its force in holding together the electrons of the unions of the chain, so that its power upon the side bonds is weakened, and therefore the atoms or groups attached to it are less strongly held, hence the greater ease with which such side atoms or groups are usually substituted. On the other hand, the nucleus of the positive atom, being repelled by that of the negative, does not exert so much of its force upon the electrons of the chain unions, with the consequence that its positive force shrinks away from these bonds and is exerted chiefly upon the side bonds, which accounts for the greater difficulty in replacing atoms or groups attached by these bonds: circumstances in many cases may, of course, modify these actions, but this is the general tendency in most cases.

<sup>1</sup> In all following demonstrations where any halides, alkali metals, hydrogen or the OH group come into a compound their octets will be omitted and instead their symbols will be given with an arrow showing their point of union.

<sup>2</sup> Refers to the groups of the periodic table.

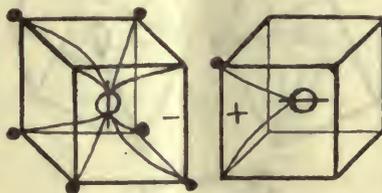
<sup>3</sup> All inner electrons have been omitted.

SOME APPLICATIONS OF THE THEORY TO  
INORGANIC CHEMISTRY.

In appraising the value of a theory it is natural to consider the more difficult cases, and especially those where the difficulties have so far been unexplained, as being the more important or more interesting; but of necessity a theory must conform to the common cases as well as the extraordinary ones: a short general survey will therefore be given, which will include some of these interesting problems in their due order.

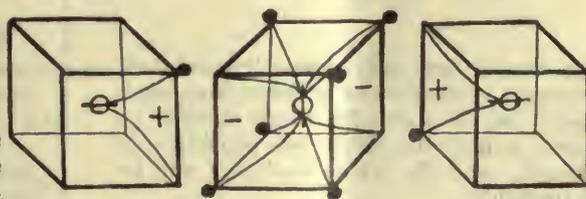
HYDRIDES, HALIDES AND HYDROXIDES.<sup>1</sup>Group<sup>2</sup> I., including Hydrogen.

General types<sup>3</sup> of the alkali halides and hydrogen halides, Fig. 1; Alkaline hydroxides, Fig. 2.



halide metal  
or  
hydrogen

Fig. 1.



metal oxygen hydrogen  
OH group  
electro-valence

Fig. 2.

In electrolytes the electron of the positive atom will pass over to the negative octet. For reasons, see *The Chemical News*, 1923, CXXVI., 133.

The hydrogen is united to oxygen, in the -OH group, by a co-valence bond, since oxygen is not strong enough in permanent polarity to wholly take over its electron; this co-valence permits the group to act as an entity; the permanent polarity of the oxygen is, however, thereby strengthened, and it can then take over the electron of a metal and form an electrovalence bond with it.

Tri atomic hydrogen will presumably be linked by partial valencies and will have the form, Fig. 3.

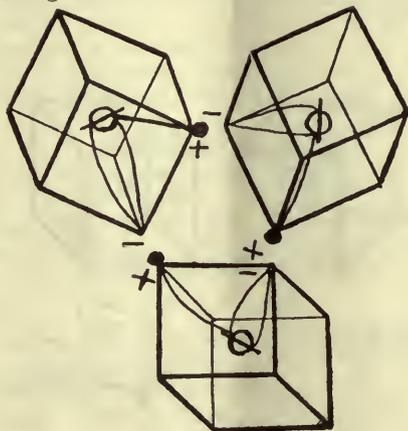


Fig 3.

The nuclei are only partially rotated, and there are three lines of force from each nucleus, where normally there should be but two, hence the three are considerably weakened, and the whole molecule will be very unstable.

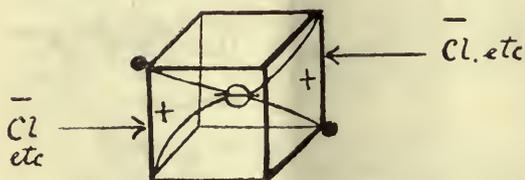


Fig 4.

## Group II.

General types of the halogen compounds  $\text{BeCl}_2$ , etc., Fig. 4; hydroxides  $\text{Ca}(\text{OH})_2$ , etc., Fig. 5.

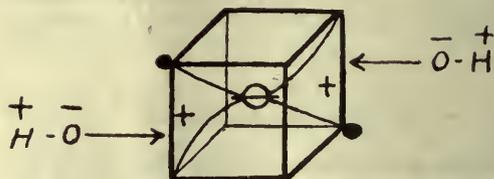


Fig 5.

These present little difficulty.

## Group III.

General types of the halogen compounds as  $\text{BCl}_3$ ,  $\text{AlCl}_3$ , Fig. 6.

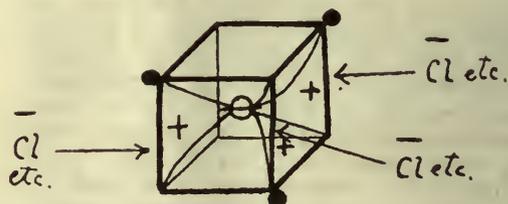
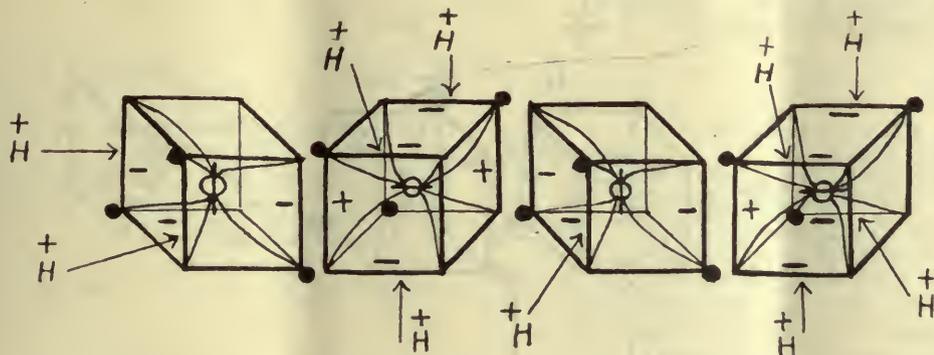


Fig 6.

The hydroxides are formed on the same plan by substituting -OH groups for halogens.

In this class, Boron forms several hydrides, notably  $\text{B}_4\text{H}_{10}$  and  $\text{B}_6\text{H}_{12}$ ; according to Stock (*Ber.*, 1912, XLV., 3539) the former, on heating to  $100^\circ$ , forms  $\text{B}_2\text{H}_6$ , which is a gas, and this, when heated at  $115^\circ$  for some time, forms  $\text{B}_{10}\text{H}_{14}$ ; he expresses surprise that these are formed and not  $\text{BH}_3$ ; but according to this theory these compounds are just what might be expected. Boron evidently has a tendency to unite with itself like carbon, therefore  $\text{BH}_3$  is not formed.  $\text{B}_4\text{H}_{10}$  will have the composition as indicated in Fig. 7, the cubes representing the boron atoms. It appears as an open chain.



or

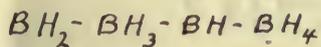
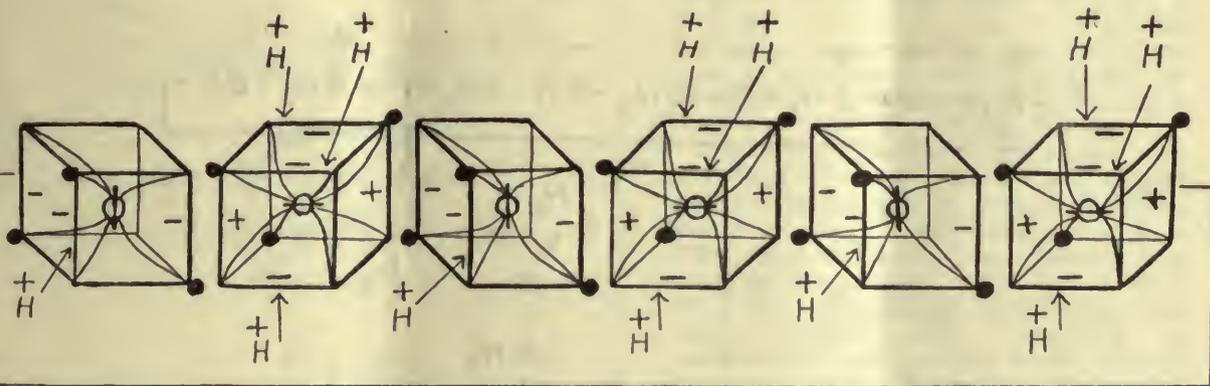


Fig 7.

$B_6H_{12}$  will appear as a ring, Fig. 8, all the bonds being single ones.



or

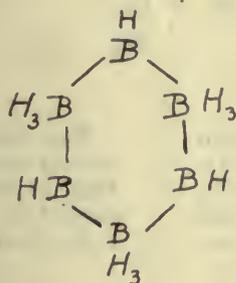


Fig 8.

$B_{10}H_{14}$  is a ring compound containing three double bonds. A double bond between two atoms of this element (see Fig. 9),

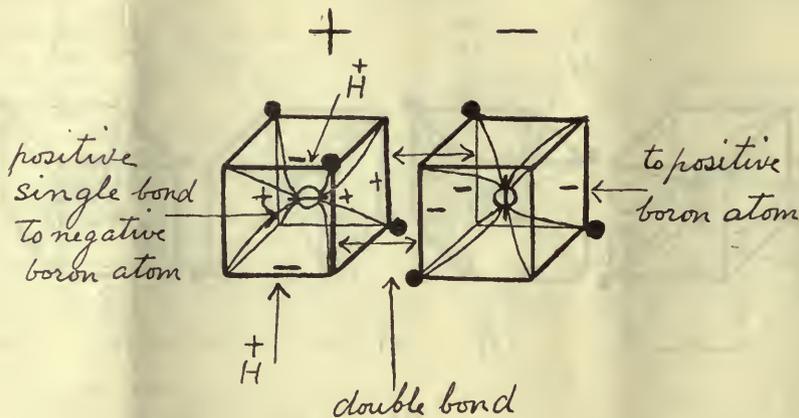
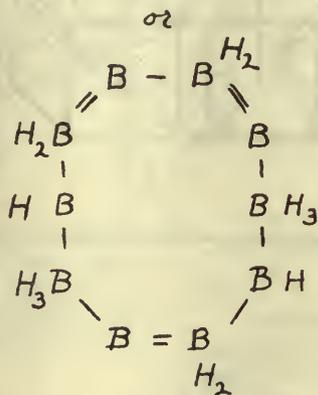
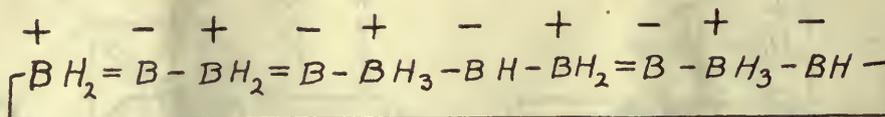


Fig 9.

leaves two negative bonds in the positive atom, but none in the negative atom; also from Fig. 8 it will be seen that in two atoms united by a single bond, the positive

atom has three spare negative valencies and the negative atom only one; we can then write the formula—



in which it will be seen that the boron atoms are alternately tri and penta valent. It must be conceded that boron may be penta valent, otherwise these formulæ cannot be constructed: it is impossible to construct any on a purely tri valent basis.

The above formula can be seen more clearly on drawing out the octets and putting in the lines of force, which was the method by which the author arrived at it. B<sub>2</sub>H<sub>6</sub> is as follows:—

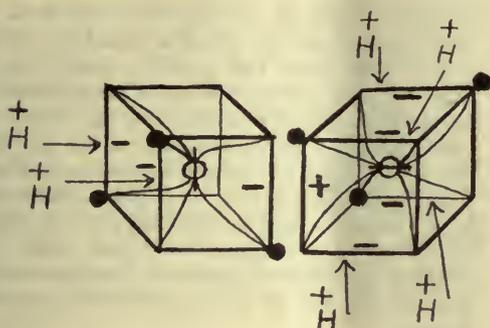


Fig 10.

It may be written  $\overset{-}{\text{B}}\text{H}_2\text{-}\overset{+}{\text{B}}\text{H}_4$ .

In all these boron hydrides it will be noticed that both positive and negative bonds come into play in the same atoms they are therefore unstable (see rule 2)\*

#### Group IV.

General types, as  $\text{CH}_4$ ,  $\text{SiH}_4$ , etc., Fig. 11;  $\text{CCl}_4$ ,  $\text{SiCl}_4$ , etc., Fig. 12.

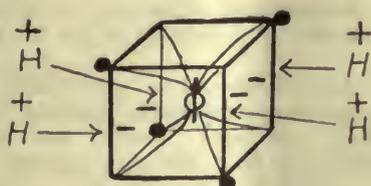


Fig 11.

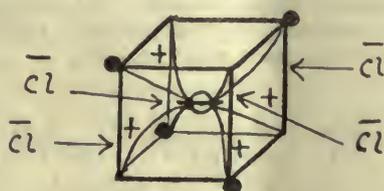


Fig 12.

(To be Continued.)

## IS THERE AN ELEMENT OF ZERO ATOMIC NUMBER?

### II.

By F. H. LORING.

In this Journal, May 18th, the subject of the above title was discussed. It was assumed that when dealing with series numbers, they should, if possible, be completed to their origins. Two series were given, and in each case when they were completed as far as possible to their origins, i.e., without passing into negative values, they seemed to imply that an element should exist with zero atomic number; but there were other reasons given for doubting this possibility. The subject, however, merits further treatment.

It is of interest to consider this problem in its more realistic aspect. Numbers alone will not carry the argument very far. The figures shown in the scheme on page 307 had in themselves no remarkable significance; indeed, other numerical sets could be given, but the point made was that if there were two active elements preceding helium—hydrogen and one other—then the series as constructed ran 0, 1, 2, 3, etc., instead of 1, 2, 3, etc., as would be the case if there was only *one* preceding element.

Atomic numbers, as is well known, are intimately bound up with the net nuclear charge of the atom, and since this is positive the number is thus associated with a charge opposite to that of an electron. This being so, the question arises—Where does the unit positive charge representing unit atomic number reside? According to modern views based largely on the work of Rutherford, this unit would be the proton, and it resides in, or is, the hydrogen atom apart from its single electron exteriorly situated. Since the hydrogen atom can now be placed in the periodic table (see references in previous paper) and it is possible to remove from it its single electron, it is not stretching matters to regard the proton as properly classified, especially since the atomic numbers are nuclear magnitudes. The electron belonging to hydrogen can thus be ignored in the placing of the nuclear magnitude, the proton.

The electron, however, is not as yet placed, and since it cannot function by itself as a positive entity, like hydrogen minus its electron, it is natural to conclude that it cannot possess a normal atomic number, though it may enter into the nuclei

\* For rules see Part I. of this series (The Chemical News, 1923, CXXVI., 263).

of atoms and condition them in terms of atomic number.

It may be jumping to a wrong conclusion to give the electron a zero number, but it is quite as reasonable a proposition as the assigning of its opposite type, the proton, to the hydrogen place, for in the latter case the hydrogen atom normally takes with it an electron. It might also be argued that since the atomic numbers are essentially positive electrically, the electron, if placed in any scheme, should have a negative place and not a neutral one, as represented by a zero number.

As a further consideration it is well to remember that the net nuclear charges of the atoms are to all practical intents and purposes their atomic numbers; and, therefore, the periodic scheme is one involving the classification of atomic nuclei. The nucleus is in fact the predominant conditioning or controlling factor in the atom; and the properties of all atoms seem to rest upon this nuclear magnitude as the sort of foundation on which the superstructure of the atom is built. The atomic numbers are magnitudes which govern the number and disposition of the external electrons that function in valency phenomena.

Another point to be considered is that in all the relations studied which involve protons and electrons there appears to be only one foundation, as it were, in the structural characteristics of matter, and all variations are due to those relative to that foundation. There are not two distinct electricities, but only one by comparison which may vary from zero to a maximum value representing positiveness, the electron being the agent of entity which brings about this change. If this is so, there can be no such thing as a negative atomic number, for the asymptotic limit, so to speak, is zero. The electric agent which brings about this change, the electron, cannot do more than neutralise a positive charge until it is practically zero. Since the relations studied are relative, this dual oneness of affairs is difficult to understand, and what appears to be a negative charge pure and simple must perhaps be judged in its relative aspect.

It is not possible to pass through zero with atomic numbers, but the negative electron may be given the zero place in the system of representation, inasmuch as it can, in its most advantageous position, only neutralise a single unit positive charge to zero. It is true that the picture can be represented in the reverse way, making the

electron the main factor, but this does not harmonise with the atomic number conception based upon the positive charge of the nucleus of the atom which is fundamentally associated with its mass; or, at least, the discussion, to be consistent, must be from the standpoint of atomic numbers. Therefore, from the relative view given, there can be no *negative* atomic number, but it might represent zero charge; in which case the electron could be taken as a *zero-producing* quantity so far as atomic numbers are concerned.

It must be remembered that the series given on page 307 implies that the zero-atomic-number element is *active* yet without a positive charge. The electron is certainly active in the chemical sense, as it serves as a bond of union in chemical combinations, and it is without a positive charge—it is relatively negative in fact, for its addition to a positive nucleus reduces the charge as already discussed.

The conventions of language involving terms denoting *opposites* should be used cautiously, as it is the phenomena which should be pictured rather than the descriptive words as such (see notes below).

There is another development in this connection as discussed by Rutherford and by Eddington, affording a further view which will be developed in the next section.

*Notes.*—It should be appreciated that the process of electrification consists in transferring electrons from one body to another. An electric current is a flow or drift of electrons. The positive charge appears always to be associated with matter in that the charge appears in proportion as electrons are separated from matter, the term *matter* here referring to the protonic structure in which the main mass resides.

#### DISINFECTANT FLUID, TALLOW AND LINSEED OIL REQUIRED IN SOUTH AFRICA.

Mr. W. G. Wickham, H.M. Senior Trade Commissioner in South Africa, reports that the South African Railways and Harbours Administration, Johannesburg, are calling for tenders to be presented by Monday, May 28, 1923, for the supply of disinfectant fluid during the period 1 July, 1923, to 31 December, 1923 (Tender No. 441).

A copy of the tender form, specification and conditions of tender, can be inspected by British firms at the Department of Overseas Trade (Room 52), 35, Old Queen Street, Westminster, London, S.W.1.

The same Administration are calling for tenders, to be presented by Monday, June 4, 1923, for the supply of tallow, and also anti-friction grease, during the period July 1, 1923, to June 30, 1924 (Tender No. 448).

A copy of the specification, etc., may be seen at the Dept. of Overseas Trade (Room 53).

The South African Railways and Harbours Tender Board are calling for tenders, to be presented by Monday, May 28, for the supply of raw and double boiled linsced oil for the six months ending December 31, 1923 (Tender 439).

A copy of the specification, general conditions of tender, etc., may be seen at the Dept. of Overseas Trade (Room 53).

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### THE ROYAL SOCIETY CONVERSAZIONE.

The following exhibits were shown on the occasion of the annual conversazione, held on May 16:—

DR. HELE-SHAW, F.R.S.: *Stream Line Filter.*

The Stream Line Filter, as its name indicates, causes the fluid which has to be filtered to flow with stream line motion. This is done by forcing the fluid between parallel sheets in a pack of such sheets made of material impervious to the fluid itself.

The space between the sheets can be regulated at will in such a way as to obtain films so attenuated that the matter in suspension, however minute, can be prevented from entering the interstices between the sheets.

The sheets may have a matted, or more or less rough, surface, but if the sheets are smooth a stream line pattern may be embossed on them either by dies or surface printing. The employment of sheets of a suitable kind of paper gives a simple and inexpensive filter for laboratory and other work, the filtrate being drawn from one tap and the residuum from another. The filter can be washed out without opening it.

THE GOVERNMENT LABORATORY (DR. FOX): *Nephelometer with Observation Tubes of Fixed Height.*

Two tubes of the same dimensions, containing the turbid liquids to be compared are placed in the path of a beam of light. Over the tubes and at right angles to the direction of the light are two Nicol prisms which can be rotated to adjust the zero. The polarised beams of light pass into separate total reflecting prisms arranged to reflect the light into planes perpendicular to each other. The beams then traverse a Lummer-Brodhun cube, and are brought into a rotatable Nicol prism through which the emergent beam enters the observation tube.

PROF. J. T. MACGREGOR-MORRIS and PROF. E. MALLETT: *Sand Figures showing the numerous resonant modes of Vibration of Telephone Receiver Diaphragms.*

A telephone receiver whose diaphragm is arranged in a horizontal plane is excited with alternating current supplied by a thermionic valve oscillator.

Sand is sprinkled on the diaphragm, and, as the frequency of the alternating current is progressively raised, the various modes of mechanical resonance appear with great sharpness. (Chladni's figures.)

At least seven modes of vibration are shown within the limits of audition. The frequencies of these have been compared with those obtained from both the membrane and the plate theories, and a graph is shown of the results.

SIR WILLIAM BRAGG, F.R.S.: (1) *Models showing Structure of Tartaric and Racemic Acid* (Mr. W. T. Astbury). (2) *Model showing arrangement of Molecules in Basic Beryllium Acetate.*

MR. E. E. BROOKS: *Photographs of Lines of Electric Force.*

Certain of the aniline dyes suspended in a dielectric liquid such as turpentine are found to give a very fair map of the electric field. The photographs shown deal with the more important special cases.

THE ROYAL SOCIETY: (1) *Centenary of Death of Dr. Edward Jenner.*

Certificate of candidature of Dr. Edward Jenner, elected a Fellow of the Royal Society, 1789.

(2) *Early Meeting Places of the Society.*

Photographs of Engravings showing the earlier meeting places of the Royal Society, namely, Gresham College (1660-1666 and 1673-1710), Arundel House, Strand (1666-1673), Crane Court, Fleet Street (1710-1780), Somerset House (1780-1857), Old Burlington House (1857-1873).

PROF. H. C. H. CARPENTER, F.R.S.:  
*Large Aluminium Crystals.*

Test pieces prepared from sheets and round bars, consisting of minute crystals—about 3,500,000 per cubic inch—have been converted into single crystals over the parallel portion of the test piece by a combination of mechanical strain and thermal treatment. When subjected to tensile stress these crystals become deformed in a peculiar way which depends, in the case of the sheet, on the orientation of the crystal. The round bars pull out so as to give a double groove instead of a cup and cone fracture as obtained from the microcrystalline test pieces. Remarkable twinning effects are also observed.

THE SCIENCE MUSEUM: *Copies of some Early Scientific Instruments.*

(1) The "Merkhet" or instrument used by the horoscope priests of Ancient Egypt to lay out temple axes, and to determine the hours of the night. *Circ.* 700 B.C.

(2) An Egyptian Waterclock from Karnak for recording the hours of the night by the fall of the water surface. *Circ.* 1400 B.C.

(3) An Egyptian Waterclock from Edfu for recording the passage of the hours by means of a rising water surface. Ptolemaic Period.

(4) A Roman Groma constructed from drawings and details supplied by Cav. Mateo Della Corte, Director of Excavations at Pompeii.

INTERNATIONAL WESTERN ELECTRIC COMPANY:

(1) *Watercooled Vacuum Tubes.*

This vacuum tube is of the same type as those used in the recent Transatlantic telephony test. A special feature of this tube is the copper-glass joint. Some parts showing the construction of the tube are also exhibited.

The photographs show a 100 Kw. tube and also some 10 Kw. tubes mounted ready for operation. Curves are also given showing the relation between Transatlantic signal strength and interference.

(2) *A Low Voltage Kathode Ray Oscillograph (in operation).*

The instrument consists of a glass tube in which a kathode ray is generated between a hot filament kathode and a small tubular anode. The ray is rendered visible by striking a fluorescent screen at the end of the tube. It is deflected with the help of two pairs of parallel plates set at right angles between which the ray passes. To the two pairs of plates two alternating potentials are applied: the fluorescent spot then traces out a curve which is a graph of the relation between the two potentials.

(3) *Rochelle Salt Piezo-Electric Crystals.*

A Rochelle salt crystal suitably mounted is shown used as a gramophone transmitter. The vibrations on the records are transmitted through the needle and cause deformations of the crystals. The deformations produce corresponding alternating differences of potential which, when applied to a telephone receiver, will reproduce the music very faithfully. The crystal is reversible and can be used as a loud speaking receiver. If alternating differences of potential are applied to the crystal the corresponding deformations can be made to cause air vibrations by suitably fitting a paper cone to it.

## MR. CONRAD BECK:

(1) *A New Illuminator for Opaque Objects under the Microscope.*

A development of the principle of the old Lieberkuhn, but consisting of an aplana-tic ring of glass silvered on back surface, enabling a short focus reflector of great light intensity to be used with powers as high as 4 mm. (1/6). The same illuminator can be used on powers from 40 mm. to 8 mm., a special type being made for 4 mm.

The objects shown illustrate its use with and without polarised light.

The latter method removes the glare caused by reflection at the object and enables true colours to be observed.

(2) *Illumination of Ordinary Objects with Polarised Light under the Microscope.*

Amphipleura Pellucida resolved into dots—1.4 N.A. Beck apochromatic object glass—immersion condenser full axial cone of light—crossed tourmalines—approximate size of dots 1,200,000 inch.

(a) Dark ground, illustrating advantage for distinguishing colour—method employed by Sir Herbert Jackson, F.R.S.

(b) Without dark ground, for resolving fine structure.



It was shown by Sir Herbert Jackson that this method enables the full resolving power of the microscope to be realised. Direct light is almost extinguished, and advantage is taken of the elliptically polarised light reflected from fine elements of structure, thus eliminating all glare, which has been demonstrated by Mr. Conrad Beck to be mainly due to reflections from the glass and slip.

**THE CAMBRIDGE AND PAUL INSTRUMENT CO., LTD.:** *A method of running a direct-current motor under a variable load, or on a variable voltage, in synchronism with a tuning fork.*

A phonic motor, designed by Dr. A. B. Wood, which is driven by a tuning fork (50 V.D.), moves a contact on a circular rheostat, the latter being rotated by the motor which it is wished to control. If the latter gains or loses speed relatively to the phonic motor, the rheostat is adjusted automatically to correct the speed of the motor.

The mechanism exhibited forms the driving part of a Plotting Chronograph designed by Dr. W. Rosenhain, F.R.S., and is exhibited by the courtesy of the Director of the National Physical Laboratory.

**NATIONAL INSTITUTE OF INDUSTRIAL PSYCHOLOGY (DR. C. S. MYERS, F.R.S.):** *Examples of Research Work*—(1) *Investigations in a Coal Mine* (MR. ERIC FARMER); (2) *Specimen Curves of Improved Output and Wastage* (DR. G. H. MILES and MR. ERIC FARMER); (3) *Intelligence Tests* (DR. CYRIL BURT); (4) *Vocational Selection Tests for Entrants to the Engineering Trades* (MR. M. H. TAGG).

**MESSRS. J. J. GRIFFIN & SONS, LTD.:**

(1) *The "Boys" Integrating and Recording Gas Calorimeter.*

In this calorimeter, which is of the water flow type, the water used is measured and doled out positively at such a rate that it will be heated 10° C. by the combustion of half a cubic foot of gas per hour if the gas is of the "declared" value, whatever that value may be. The gas is doled out positively at atmospheric pressure at that rate corrected for temperature, pressure and contained water vapour accurately to one part in 1,000. The means used for adjusting the rate are a ball-cylinder-disc integrator and epicyclic gearing, called the thinking machine. A recording drum and driving gear of extremely simple construction keep a record of the ever-changing volume

factor of the gas. The heat interchanger of folded sheet lead autogenously soldered is also a new construction, as is the method used for the soldering. The operative thermometers are brass boxes with elastic accordion tops filled with amyl alcohol. These through a lever system working in three dimensions of space, operate a pen moving one inch for each degree centigrade. This rests on the middle line of the chart if the gas is of its declared value, and it moves one-tenth of an inch for each 1 per cent. of increase or decrease. An Amsler integrating wheel gives the average value since it was last set. The paper is ruled and marked in half-hours, days and half-days as it passes through the machine. Distilled water produced by an automatic still only is used, and this is circulated and cooled by the operation of a small hot air engine. The one-wheel clock which governs all the mechanism is driven by the waste water.

(2) *New small "spot test" Calorimeter.*

This is the meter and interchanger of the recording instrument adapted for personal observation. The final temperature is reached in 10 minutes from lighting the gas, and the tiresome meter proving operations are not necessary.

**MR. D. NORTHALL-LAURIE:** *Photomicrographs of Crystals in Colour mounted to show changing tints.*

When crystals are examined under a microscope with polarised light with the addition of a selenite plate cut of such thickness to show a green colour and a red colour when rotated through an angle of 45°, the predominant tint changes from green to red. The Paget viewing screen used for the Paget colour photographic process being composed of minute squares of green and red, neglecting for the moment the smaller blue squares, enables it to be possible by changing the register of the viewing screen when combined with the transparency to imitate on the lantern screen the effect produced when using polarised light. Colour photographs are taken of the subject and the slides are so constructed to allow of the viewing screen being slowly moved across the transparency. In this manner the tint of the slide changes from green through various intermediate colours to red, depending upon the relative position of the slide and screen. Various slides of subjects suitable for exhibiting this effect have been constructed on this principle.

## THE NATIONAL PHYSICAL LABORATORY:

(1) *Iron Mercury Calorimeter* (DR. EZER GRIFFITHS and MR. F. H. SCHOFIELD).

The calorimeter consists of a cylindrical block of iron with a hole for receiving the specimen and a lid which serves also as a container of mercury. Arrangements are made for flooding the hot specimen with mercury. The apparatus is particularly useful for dealing with materials of low thermal conductivity or materials which react with water.

(2) *X-Ray Spectra of Alloys* (DR. E. A. OWEN and MR. G. D. PRESTON).

Spectrographic curves showing the atomic structure of pure metals and alloys. The method depends upon the presence of a large number of small crystals in plates of the material. The effect is enhanced by polishing and etching.

(3) *Photomicrographs of Woods* (DR. G. W. C. KAYE and MR. W. F. HIGGINS).

Certain woods of low density, viz., *Ochroma lagopus* (Balsa wood), *Apeiba tibourbou* and *Paulownia imperialis* (Japanese Kiri wood), have been found to possess very low thermal conductivities. Photomicrographs of these are shown side by side with those of pine and beech, and the marked difference in the thickness of the cell walls is easily seen.

MR. E. HATSCHKE: *Imitations of Organic Forms by Drops and Vortices of Gelatin.*

Permanent "hanging drop" and vortex forms can be obtained by allowing gelatin sol to run into suitable coagulating solutions, the temperatures and densities being so adjusted that the gelatin sets when the desired form has developed. Owing to shrinkage a number of features, such as radial ribs, undulating membranes, stellate and crenated discs, etc., appear, which are absent in liquid models. Further modifications can be introduced by causing permeable or semi-permeable membranes to form at the proper time; models of the red blood corpuscle and segmented forms are produced by this procedure.

PHYSICAL DEPARTMENT, ROTHAMSTED EXPERIMENTAL STATION, HARPENDEN: *Flocculation and Deflocculation in Soils.*

The phenomena of flocculation and deflocculation are of great importance in soils, as they are associated with the formation of

tilth. The experiments include measurements of the volume changes of soil resulting from alterations in its moisture content, and a demonstration of the influence of lime on the flocculation of soil samples taken from successive depths of an experimental plot. The automatic electrical balance, devised by Prof. Oden and Dr. Keen, furnishes a continuous time record of the accumulating weight of deposit from a soil suspension. Analysis of the time-weight curve thus obtained, leads to a distribution curve showing the relation between the weight (or number) of particles and the effective radii; the shape of the curve varies according to the degree of dispersion of the soil suspension.

Certain practical consequences are illustrated by means of dynamometer record-charts of draught of ploughs under different conditions.

[Shown by Dr. B. A. Keen, with Mr. E. M. Crowther and Mr. W. B. Haines.]

MR. F. HARRISON GLEW: *A Levitating Magnet.*

This experiment shows a bar magnet of cobalt steel, floating by repulsion above the opposed poles of a fixed magnet, at a vertical distance of half-an-inch, or more, according to the strength of the magnetic field.

The floating magnet is free to move vertically and may be made to oscillate up and down in its glass enclosure. The experiment fails with ordinary magnet steel, as reversal of polarity takes place in the intense magnetic field necessary for flotation.

NATIONAL INSTITUTE FOR MEDICAL RESEARCH (DR. LEONARD HILL, F.R.S., and DR. A. EIDINOW): *Effect of Temperature on the Biological Action of Light.*

DR. W. LAWRENCE BALLS, F.R.S.: *Mirror-Image Structures in Cell-walls of Cotton Hairs.*

The cotton hair has a characteristic convoluted form; these convolutions have long been known to be both right and left-handed in any one hair. Such reversals of the external spiral are primarily due to reversals of a spiro-fibrillar internal structure in the cellulose wall, these in their turn being due to growth-causes as yet unknown.

The preparation is a longitudinal section of a cotton hair, through a reversal. The single layer of wall thus observed between

crossed nicols, with light elliptically polarised through quartz plates, shows the structural reversal clearly by a change in the interference colours. If now the circular stage of the microscope be rotated, it will be found that the positions of maximum extinction are also reversed on either side of the micro structural reversal, the optical axes being thus related to the spiral-fibril axes, and not to the cell-axis. This indicates the existence of a definite pseudo-crystalline space-lattice structure.

NATIONAL INSTITUTE FOR MEDICAL RESEARCH (DR. E. H. J. SCHUSTER): *A New Recording Kata-Thermometer.*

Mr. E. B. MOULLIN: *A Direct Reading Thermionic Voltmeter.*

The voltmeter employs the rectifying property of the Thermionic Vacuum tube. If an alternating P.D., whose mean value is zero, is applied between grid and filament, a current is produced in the anode circuit whose mean value is not zero. The value of the current so produced is used as a measure of the alternating P.D. applied to the instrument. The exact conditions obtaining at the time of calibration are readily reproduced in a simple manner.

The readings of the instrument are unaffected by the frequency of the applied alternating P.D., and experiment shows that if this frequency is changed from 10 per second to a million per second, the error produced is less than 2 per cent.

The electrostatic capacity of the voltmeter is of the order of 20 oms and the power it absorbs at full scale is about 50 ergs per second.

Mr. GEORGE H. GABB: *Bust of Galileo, carved in pear wood. Probably a work of about 1650-70.*

This bust, formerly in the Methuen Collection, is rather larger than life size, and stands 39 inches high.

The sole consists of a group of astronomical emblems, carved in high relief; surmounted by a globe, around which, in a belt, are carved the Signs of the Zodiac.

At the back of the bust, in a circular glazed recess, is preserved a relic of Galileo; a piece of crimson velvet, with silk fringe, possibly a piece of the covering of his academic chair.

This has been removed carefully, and was shown in the small glass case.

Mr. WALTER HEAPE, F.R.S.: *Exhibition of three series of photographs illustrative of the following:—*

(1) Heape and Grill's rapid cinema machine designed to take photographs at rates from 500 to 5,000 per second. (This machine is now in use at Shoeburyness for recording the results of gunnery experiments.)

(2) Film photographs taken at the rate of 2,500 per second of a 15 in. glass vacuum globe (Osran) broken by a hammer. (This shows what occurs during the complete break up of the globe in about one-twentieth of a second.)

(3) Film photographs taken at the rate of 2,000 per second of a 5 in. solid rubber ball weighing 2½ lb. shot from the mouth of a 2 1/16th in. diameter gun against a steel target.

They show the extraordinary contortions of the ball from the instant when it is shot off a tee by the head of a tom-pion fixed in the mouth of a gun until it rebounds from the target—that is, a flight of about 1/40th of a second.

Mr. H. J. BUCHANAN-WOLLASTON: *On the Value of Markings on Herring-Scales as a Means for Estimating Age and Growth Rate of the Fish.*

Mr. PERCY R. LOWE: *Variation in Red-Legged Partridges (*Alectoris rufa*).*

Mr. H. GRAHAM CANNON: *Beetles showing transplanted heads.*

Prof. J. W. GREGORY, F.R.S., and Mr. C. J. GREGORY: *Fossils from the Devonian, Carboniferous and Triassic Rocks of Chinese Tibet.*

The collections were made by Prof. Gregory and Mr. Gregory during the Sladen Trust Expedition, 1922.

DEPARTMENT OF ZOOLOGY, BRITISH MUSEUM (NATURAL HISTORY) (Mr. C. TATE REGAN, F.R.S., and Mr. M. A. C. HINTON).

(1) *Deep-sea Cables Damaged by Shark Bites*; (2) *Contents of a Crocodile's Stomach*; (3) *Modifications of the dentition in some African Vertebrates.*

BOTANY SCHOOL, CAMBRIDGE (Mr. JOHN WALTON): *A New Method of isolating Mummified Fossil Plants for purposes of Microscopical Examination.*

THE DIRECTOR, ROYAL BOTANIC GARDENS, KEW:

(1) *Efwatakala Grass—Melinis minutiflora* P. Beauv.

(2) *Rubiaceous Plants with Bacterial Nodules in the Leaves.*

MR. H. TAVERNER: *Stereo-photo Micrographs of Hydracarina (Water Mites) in Natural Colours.*

RESEARCH DEPARTMENT, WOOLWICH: (1) *Detection of Feeble X-ray beams by Smoke Clouds.*

In this method a smoke cloud, having a flat top, is produced in a small chamber, and above this cloud is placed an electrode maintained at a potential about 400 volts above earth. The cloud is then interposed in the path of an X-ray beam, and some of the ions thus produced attach themselves to the smoke particles, which are then drawn up from the top of the cloud under the influence of the electro-static field.

The movement of these particles is observed by an ultra microscope. The exhibit illustrates the application of the method to the detection of feeble X-ray beams reflected from crystals.

(2) *Chronograph, for use with a photographic Recorder.*

(3) *Autographic Recording of Dilation of Solids at High Temperatures.*

MR. S. G. BROWN, F.R.S.: *The Frenophone.*

MESSRS. ADAM HILGER, LTD.: *Optical Apparatus for Research.*

(1) Vacuum Grating Spectrograph for photography of the Schumann and Lyman Regions.

(2) Diffraction Gratings ruled at the National Physical Laboratory.

(3) Interferometer for measuring the aberrations of lens systems.

(4) Lummer Gehreke Parallel Plate with resolving power of 850,000. Made for the Physical Laboratory of the University of Toronto.

(Shown by kind permission of Prof. J. C. McLennan, F.R.S.)

NATIONAL INSTITUTE FOR MEDICAL RESEARCH (MR. J. E. BARNARD, MR. JOHN SMILES and MR. F. WELCH):

(1) *Improvements in the method of Mi-*

*croscopical Observation known as "Dark-ground Illumination."*

(2) *An Experimental Demonstration with the Microscopic Interferometer.*

The Microscopic Interferometer is intended for the double purpose of testing microscope objectives and similar optical combinations, and for use as a microscope of high accuracy.

The experiments shown indicate the effect of alteration of tube-lengths on the zonal corrections of an objective. As the illuminant used in this case is a mercury vapour lamp, the demonstration is confined to the three brightest colours emitted by mercury vapour.

When used as a microscope the accuracy of the fine-adjustment motion is some ten times greater than in any ordinary microscope. Thus, if ultra-violet light is the illuminant, successive images in any single wave-length can be obtained with precision.

DR. IRVINE MASSON: *Apparatus for Measuring the Compressibility of Gases.*

The body contains four holes, communicating with each other and with a space in which a plunger works through a special gland. The cavity is full of mercury; in each hole is set a glass tube filled with about 15 cc. of gas. By screwing in the plunger the mercury forces the gases into the visible capillary portions of the tubes where their volumes are measured, the capillaries having previously been calibrated. One tube contains a standard gas and thus serves as an accurate pressure-gauge.

The advantages of this form of Andrews' original pattern lie chiefly in its freedom from leakage at high pressures and in its capacity for four samples at once. It has been used at 450 atmospheres' pressure.

ANGLO-PERSIAN OIL Co., LTD.: *Lubricating Oils under Electrostatic Stress.*

The Electrostatic Stress is applied by means of a disc of brass resting on the smooth surface of a piece of lithographic stone, commonly called printer's stone.

The metallic disc is connected to a negative source of supply of 105 volts whilst the stone is connected by a copper plate (on which it rests) to the opposite pole of the supply.

Under these conditions, it can be shown by a balance system of suspension that the

electrostatic stress is capable of supporting a considerable weight.

If the smooth surface of the stone is covered with a thin film of lubricating oil, and the potential difference applied as before, a decrease in the electrostatic pull is observed; this pull varies with different oils.

SIR RICHARD PAGET, BART., gave a demonstration on *The Nature and Reproduction of Vowel Sounds*. MR. WALTER HEAPE, F.R.S., also gave a demonstration on *Cinematograph Exhibition*. A series of films, the photographs of which were taken at rates varying from 2,000 to 3,000 per second.

### THE ROYAL SOCIETY.

THURSDAY, MAY 17.

Papers read:—

A. E. H. TUTTON, F.R.S. (1) *A Universal Interferometer*. (2) *A Wave-length Torsometer, and its Use with the Universal Interferometer*.

(1) The instrument is an interferometer of general application, for the measurement of very short distances, small deformations or changes of dimensions, or minute amounts of motion, by the interference-band scale of half wave-lengths of light. It was suggested by the success attained with the comparator for standards of length, designed for the Standards Department of the Board of Trade, and described to the Royal Society in 1909.

Its essential feature is a travelling microscope driven by a specially constructed fine screw along a very true V-and-plane guiding bed, so steadily that one of the two glass reflecting surfaces concerned in producing the interfering monochromatic light rays is actually carried rigidly with it, so that the amount of its motion is measured directly in interference bands. The microscope and its mountings, the large driving wheel which works the fine screw by means of a connecting flexible shaft, endless screw and worm-wheel, are similar to the pair of microscopes carried by the standards comparator, but the one microscope is more conveniently arranged for the special purpose in view, and has several minor improvements, including better resolution of Grayson-ruling fiducial

marks, combined with greater working distance, and more convenient lighting of these 40,000 to the inch rulings.

The interference apparatus is practically identical with that of the comparator, consisting of the same type of autocollimating telescope with micrometer eyepiece, and vacuum tube on the elbow tube, a constant deviation prism for the selection of the monochromatic radiation to be used, and large truly worked glass interference discs. The telescope is mounted to the right, and the driving wheel to the left, and the 30-inch long V-and-plane bed, in its rigid carrying plinth-bed, is supported on pillars at the Airy positions for no flexure, the whole being counted on a heavy solid rectangular base. The large middle space on the latter, and that underneath the arch, are available for the accommodation of whatever object, or apparatus carrying the object and possibly causing its motion, is brought to measurement. A large circular work-table, provided with every possible requirement of adjustment, is supplied in this clear middle space, for the convenience of the support of the object or its manipulating apparatus.

(2) This is a refinement of the Voigt instrument for determining the torsion constants of miniature bars of crystals and other small bodies. The essential difference is that the two optical levers of Voigt are replaced by radials which move the two sliders carrying Grayson-ruling fiducial marks, referred to in the preceding communication. The new torsometer is essentially composed of a miniature lathe-bed, carrying two similar but mutually reversed wheel-and-chuck fittings, the chucks for gripping the object bar ends, and the wheels, which move solidly with the chucks, for delivering the force-couple at one end and holding it firmly at the other, the two ends being interchangeable, either wheel being capable of locking fixation or of driving by a power band. The band passes round the lower half of that pulley-wheel on a standard. The end depending from in front of the latter terminates in a loop of the cord-band, into which the hook carried by the weight can be allowed slowly to fall, until the whole weight is acting in twisting the object bar. The apparatus of Voigt for bringing the weight into action is replaced by the far more delicate one belonging to the elasmometer, the interference apparatus described by the author in 1904 for determining Young's modulus by the bending

of bars or plates. The weight can be delivered by this apparatus by either a coarse or a very fine movement, as required or desired.

When in use the torsometer is supported on the work-table of the universal interferometer, described in the preceding communication, where it can be rigidly clamped and delicately adjusted, so that the two aluminium radials carried by the object bar near its two ends, just clear of the chuck-grippers, are in contact near their upper terminations with the blunt knife-edge ends of the two sliders. The table adjustments permit matters to be arranged so that the Grayson-ruling signal is centred under the microscope when the radial under observation is just in complete contact with the slider. On delivering the weight and effecting the twist, the slide and signal move, and the movement is followed by driving the microscope by the big wheel of the interferometer until the signal mark is again centred, the number of interference bands effecting their transit the while being carefully counted.

L. N. G. FILON, F.R.S., and F. C. HARRIS. *On the Diphasic Nature of Glass as shown by Photo-elastic Observations.*

A block of flint glass was heated to about 400° C., when it showed some signs of softening; it was then allowed to cool under longitudinal pressure. On removing the pressure it was found to have become permanently doubly-refracting. The residual stress which should produce the observed amount of double-refraction is calculated by a new method, and the result shows that this residual stress does not balance according to the laws of statics. It is deduced that a "crypto-stress" exists, which does not manifest itself optically.

This leads to the conclusion that the glass is not homogeneous, but behaves as a mixture of two components or phases. A possible interpretation of the results on this hypothesis is put forward.

Papers read in title only:—

C. E. INGLIS. *Stress Distribution in a Rectangular Plate having Two Opposing Edges sheared in Opposite Directions.* Communicated by Prof. E. G. Coker, F.R.S.

The type of deformation dealt with in this paper may be termed a pure mechanical shear, in contradistinction to pure shear as

usually understood in stress analysis. The deformation is produced as follows:—

Imagine a thin rectangular plate bounded by two horizontal lines AB CD and two vertical lines AD BC. The two horizontal edges while remaining straight and unchanged in length and in distance from one another are displaced longitudinally in opposite directions, the vertical edges being kept free from applied stress. The plate being thin, the distribution of stress consequent on this deformation is regarded as two-dimensional and the stress components are obtained *via* solutions of  $\nabla^4 V = 0$ . Two different sets of functions satisfying this equation are evolved, and by methods of Harmonic Analysis they are combined to satisfy the prescribed boundary conditions to a high degree of approximation.

Particular attention is given to the stress distribution along the horizontal centre line. This stress starting from Zero at the free edge mounts up rapidly, and for a plate in which the length is considerable compared with the depth, the stress soon assumes a constant value; but before doing so, it overshoots this value, and the curve of stress distribution in consequence develops humps near the free vertical edges. If the length—breadth ratio of the plate is 2 to 1 these humps combine to give a flat-topped curve. If the plate is square the coincidence of the humps makes the curve approximate to a parabola.

These characteristics were first brought to light by Prof. Coker, who examined this particular stress distribution by Optical methods. The results obtained in this paper are in close agreement with his determinations. This investigation reveals the existence of large stresses at the corners of the plate, a state of affairs confirmed by reference to Prof. Coker's original coloured photographs.

T. H. HAVELOCK, F.R.S. *Studies in Wave Resistance—Influence of the Form of the Water-plane Section of the Ship.*

In these calculations the ship is represented by a vertical post of infinite depth whose horizontal section is similar to the water-plane section of a ship. Expressions for the wave resistance are developed and are evaluated in terms of Bessel and Struve functions of which tables are available. The level lines of the model are varied while the displacement is kept constant; and in this manner a comparative study is made of

such problems in ship resistance as the effect of finer lines and greater beam, and of the difference between straight and hollow lines. Numerical calculations are made for four models, and the results are shown graphically and analysed in relation to experimental data.

W. M. H. GREAVES. *On a certain Family of Periodic Solutions of Differential Equations, with an Application to the Triode Oscillator.* Communicated by Prof. H. F. Baker, F.R.S.

An application is made to the equation of Appleton and Van der Pol for the Triode oscillator. It is shown that this equation can be reduced to a particular case of the above equations, and that the series for the periodic solutions which were obtained in a purely formal manner by Dr. Appleton and the writer in a recent issue of the *Philosophical Magazine* are convergent for sufficiently small values of some of the quantities involved.

#### ROYAL INSTITUTION.

On Tuesday, May 22, PROFESSOR FLINDERS PETRIE began a course of three lectures at the Royal Institution, on *Discoveries in Egypt*; on Thursday, May 31, SIR WILLIAM BAYLISS will deliver the first of two lectures on *The Nature of Enzyme Action*; and on Saturday, June 2, DR. A. W. HILL the first of two on *The Vegetation of the Andes and the New Zealand Flora*.

The Friday evening discourse on May 25 will be given by SIR ASTON WEBB on *The Development of London*, and on June 1 by PROFESSOR H. A. LORENTZ on *The Radiation of Light*, and on June 8 by MISS JOAN EVANS on *Jewels of the Renaissance*.

#### THE CHEMICAL SOCIETY OF JAPAN.

Papers communicated:—

*The Influence of the Temperature upon the Action of Invertase, and a Theory on the Mechanism of the Action of Invertase.* by BUNSUKE SUZUKI.

*Chemical Investigation on Japanese Minerals containing Rarer Elements. Part V. Analysis of Beryl from Ishikawa, Iwaki,* by TAKU UYEMURA.

*On the Preparation of  $\beta$ -Oxymethylamine and its Salts,* by SIN-ITI KAWAI.

*The Constitution of Pyrethronic Acid,* by RYO YAMAMOTO.

#### NOTICES OF BOOKS.

*Practical Chemistry,* by E. J. HOLMYARD, B.A. Pp. XVI. + 267. London: G. Bell & Sons, Ltd., Portugal Street, W.C. 1923. Price 4s. net.

The author has divided his laboratory textbook in two parts. The elementary portion includes a wide range of simple and very suitable experiments, introducing young students to chemical principles and laws. These experiments have evidently been so chosen that general chemical manipulation and different types of operations will all be carried out in the practical study of such matters as the simple laws, equivalence, the common gases, acids, bases and salts.

The second part contains sections on more advanced experiments in inorganic chemistry, such as the more difficult preparations, and the general reactions of the metals. There is a lengthy section on Volumetric Analysis, and a few gravimetric exercises are given.

An excellent feature of this practical volume, primarily intended for use in schools, is the inclusion of a series of experiments in Physical Chemistry. These, like the others, and the twenty or so Organic Preparations given in the final section, are described with adequate detail, so that the students may be largely left to themselves to arrange the apparatus and conduct the experiments with the minimum of help.

However good a laboratory manual may be, it cannot completely supersede personal supervision in practical work, but Mr. Holmyard's textbook should prove of the greatest value in the teaching of practical chemistry. J.G.F.D.

#### BOOKS RECEIVED.

*Qualitative Organic Analysis: An Elementary Course in the Identification of Organic Compounds,* by OLIVER KAMM. Pp. VII. + 260. First Edition. 1923. London: Messrs. Chapman & Hall, Ltd., 11, Henrietta Street, Covent Garden, W.C.2. 12s. 6d. net.

*The Phase Rule and the Study of Heterogeneous Equilibria: An Introductory Study*, by A. C. D. RIVETT, M.A., B.Sc. (OXON.), D.Sc. (MELB.). Pp. 204. 1923. Oxford: The Clarendon Press. 10s. 6d. net.

*The Chemistry of the Inorganic Complex Compounds: An Introduction to Werner's Co-ordination Theory*, by DR. ROBERT SCHWARZ. Authorised Translation by LAWRENCE W. BASS, Ph.D. Pp. X. + 82. 1923. London: Messrs. Chapman & Hall, Ltd., 11, Henrietta Street, Covent Garden, W.C.2. 8s. 6d. net.

The U.S. Dept. of Agriculture have just issued a bulletin, No. 1,146, *The Influence of Copper Sprays on the Yield and Composition of Irish Potato Tubers*, by F. C. COOK,

Tubers from copper-sprayed potato plants at the time they were large enough for analysis, usually contained more solids, starch, and nitrogen than the tubers from unsprayed vines. The starch content increased approximately 50 per cent. as the tubers matured, while dextrose disappeared and sucrose was materially reduced. Early varieties of potatoes showed a decrease in their sugar content accompanying an increased starch content in the copper-sprayed tubers during the early stages of development. The proportion of insoluble ash decreased during the growth of the tubers, although the total ash content remained constant. Total nitrogen increased. The figures for soluble, coagulable, and particularly the monoamino and amide nitrogen increased as the tubers matured.

The proportion of tubers to green vines appeared to be higher for the copper-sprayed than for the unsprayed plants.

Average data for seven States in 1919 showed the food value of an acre of copper-sprayed potatoes to be 839 pounds more than that for an acre of noncopper-sprayed potatoes. Two factors, increased yield (48 bushels an acre) and an increase of solids (5.6 per cent.), are involved.

Tubers from several varieties of potatoes from a northern State were higher in solids than tubers of the same varieties grown in a southern State.

A larger yield of potatoes was secured from copper-sprayed than from check or noncopper-sprayed vines. Late blight (*Phytophthora infestans*) is eliminated as a necessary factor in the case.

When a lime spray containing no copper was used on one occasion, the yields of

tubers were decreased. Pickering-lime-water spray and a barium-water spray gave practically the same increase in yield and in solids of the tubers as a Bordeaux spray. The copper in the spray seems to be the essential factor.

*The Forty-seventh Annual Report of H.M. Inspectors of Explosives* (1922) has been issued for the Home Office by H.M. Stationery Office, Price 6d. Pp. 36.

This report deals with matters arising out of the operation of the Explosives Act, 1875. These include Inspection, Accidents, Accounts, and comments on Accidents abroad, Experiments, Use of Explosives in Coal Mines, Petroleum and Carbide of Calcium. An appendix classifies the accidents for the period.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Latest Patent Applications.*

- 11003—Agricultural Developments Co. (Pyrford), Ltd.—Manufacture of nitrogenous fertilisers. April 23.  
 11082—Borchers, W.—Process for refining crude chromium alloys. April 24.  
 11389—Borchers, W.—Ferrous alloys. April 27.  
 11110—Carbide & Carbon Chemicals Corporation.—Process of oxidising dibenzyl. April 24.  
 11000—Christensen, C. P.—Manufacture of calcareous and nitrogenous fertilisers. April 23.  
 11526—Evans, E. V.—Treating gases for removing carbon disulphide. April 28.  
*Specifications Published this Week.*  
 195998—Buehner, Dr. M.—Production of pure alumina.  
 196002—Cumming, A. C., and Klarit, Ltd.—Decolorisation and clarification of fats, oils, sugars, and other liquids, and adsorptive materials for use therein.  
 196012—Vielle, J. A.—Process for the manufacture of insecticidal and fungicidal preparations.  
 196115—Phillipson, G. A.—Process and apparatus for drying and neutralising sulphate of ammonia.

*Abstract Published this Week.*

- 194208—Phosphatic fertilisers.—Soc. Anon. Produits Chimiques et Engrais L. Bernard, Mesvin, Cibley, Belgium.

*Calcium phosphate.*—A fertiliser is obtained by heating together a homogeneous mixture of a phosphate rock, blast-furnace slag or feldspar, and bye-products containing alkalis such as residues from sugar mills or distilleries, or wool grease. The residue containing alkalis may be employed as such or may be first calcined and ground. The mixture of the materials may be effected wet or dry and the heating may be at 1,300° C.

Messrs. Rayner & Co. will obtain printed copies of the published Specifications, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3294.

## AN EXPLANATION OF THE THEORY OF THE ROTATION OF THE ATOMIC NUCLEUS.

### PART II.

By HERBERT HENSTOCK.

(Continued from Page 325.)

Carbon has been included in order not to spoil the sequence of the elements, but it is proposed to discuss organic problems separately.

The case of stannous chloride is also postponed until those cases where distortion of the octet is considered.

#### Group V.

General types, as  $NH_3$ ,  $PH_3$ ,  $AsH_3$ , etc., Fig. 13.

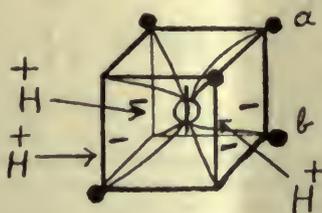


Fig 13.

In these compounds the stability decreases with increase of atomic weight, that is to say, the negative bonds are weakened or the octet electrons are not so strongly held by reason of the successive layers of inner electrons. One result of this is that the negative bond a-b (Fig. 13) in nitrogen is stronger than those in phosphorus or arsenic, with the consequence that nitrogen is more basic and so will form more stable compounds by means of that bond.

Such nitrogen compounds as  $NH_4Cl$ ,  $NH_4NO_3$ , etc., will be formed on the general equation expressed in Fig. 14.

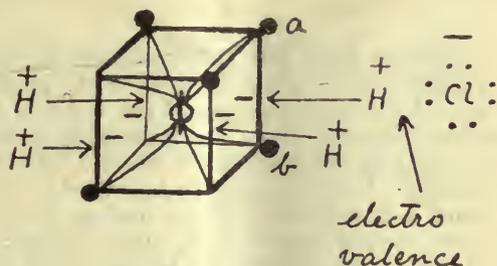


Fig 14.

The electrolyte  $HCl$  unites with ammonia by the negative bond a-b: the nitrogen in ammonia is negative in alternate polarity and is trivalent. It is a general rule, put forward by Lowry (lecture before the Faraday Society, Nov. 20, 1922), and also by Sidgwick (lecture before the Chemical Society, March 1, 1923), that when an atom shares two electrons with another, both electrons being supplied by one atom, then that atom acquires a positive charge; that is to say it loses part of its octet, and so the nucleus gains more power over the remainder. The atom which supplies no electrons acquires a negative charge, due to the extra electrons in its octet. This means that each atom slightly alters its permanent polarity, and this acts upon the nucleus of each and revolves it, making the alternate polarities change their signs. The constitution of ammonium chloride will then be represented by Fig. 15.

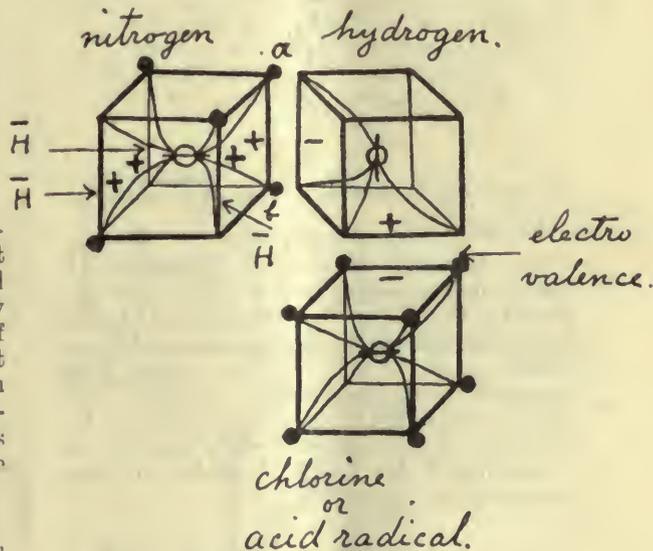


Fig. 15.

The key atom is the nitrogen, and the undoubted cause of its being so is the partial loss of the two electrons of the bond a-b, which slightly alters the permanent polarity causing the nucleus to revolve and the valency of the nitrogen to be raised. The bond a-b becomes positive and so also do those bonds uniting the three hydrogen atoms of the ammonia, whose nuclei revolve, making them negative in alternate polarity only: the nucleus of the fourth hydrogen atom also revolves, and it becomes negative, but in permanent as well as alternate polarity, hence the difference between the action of this and the other three. This fourth hydrogen atom unites with the chlorine, in the electrovalence bond, by one of its positive edges, but since it is united to the nitrogen by a normal edge therefore this union is stronger than the electrovalence bond, so that the whole of the  $\text{NH}_4$  is a fairly stable entity and can act as a group.

Ammonium hydroxide will be represented by Fig. 16.

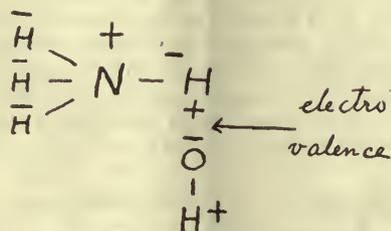


Fig. 16.

the extreme instability of which is apparent.

The fact that ammonium hydroxide is not so strong a base as the alkali metal hydroxides is due to the intervening fourth hydrogen atom with its inherent weakness where positive and negative edges both come into play (see rule 2). Organic tetra alkyl ammonium bases are as strong as the metallic alkalis, but the very simple explanation of this will be included amongst the organic compounds.

Those hydrides of the types  $\text{NH}_2\text{-NH}_2$  or  $\text{PH}_2\text{-PH}_2$  will have the general formula as in Fig. 17.

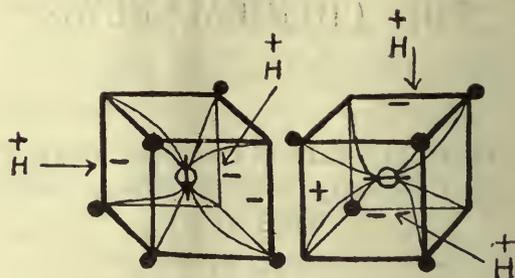
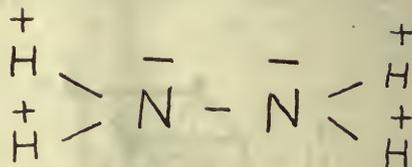


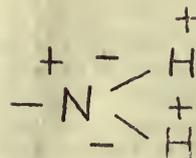
Fig. 17.

In hydrazine the positive nitrogen atom is united to hydrogen by negative edges, which makes the molecule unstable (rule 2) and accounts for this compound being less stable than those of the  $\text{NH}_3$  type.

The positive nitrogen atom is an example of how one cannot strictly label all atoms completely positive or negative. In writing



the facts are not properly expressed, for no wholly positive or wholly negative bonds ever unite two atoms, their alternate polarities must be opposite. A more explicit method would be to label the second nitrogen thus—



which would show where the weakness of the molecule lay.

The phosphorus hydride  $\text{P}_2\text{H}_6$  will be found to have the following constitution, if it be worked out in a similar fashion to those already shown for boron. It is a ring containing three double bonds, in which the phosphorus is tri valent. Thus:—

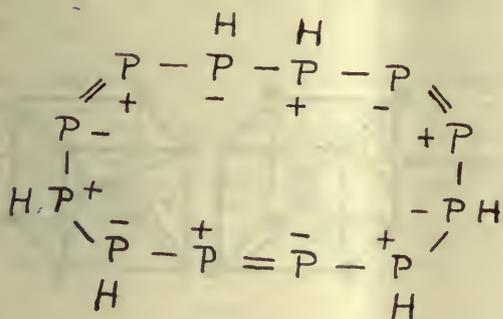


Fig. 18.

The general types,  $\text{NCl}_3$ ,  $\text{PCl}_3$ ,  $\text{AsCl}_3$ , etc., are represented:—

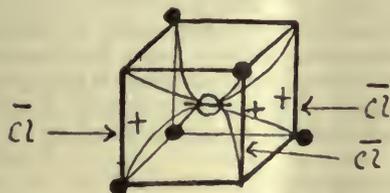
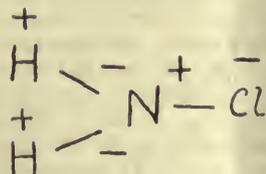


Fig. 19.

The chlorine, bromine, etc., are united to positive bonds, but nitrogen is an element fairly strong in negative permanent polarity and it is only in those compounds where the electrons of the bond  $a-b$  (Fig. 13) are shared with another element that it becomes positive and basic, hence when this bond is unoccupied the nitrogen atom tends to unite along negative edges (as in ammonia, Fig. 13), in order to form stable compounds. In the case of these halogen compounds this tendency is not fulfilled, which accounts for the extreme instability of  $\text{NCl}_3$ , etc.

Mono chlor amide will have the constitution—



where the nitrogen is united by negative

edges to the hydrogen and by a positive edge to the chlorine: the molecule is therefore unstable (rule 2).

The general types,  $\text{PCl}_5$ ,  $\text{AsCl}_5$ , may be constituted as shown in Fig. 20.

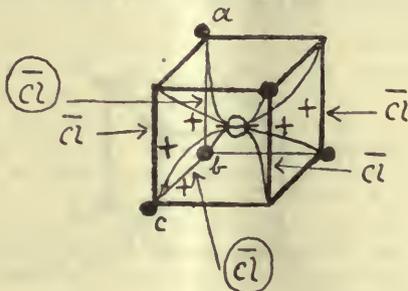


Fig. 20.

The two chlorine atoms in the rings are the two extra ones, and they may unite with the positive bonds  $a-b$  and  $b-c$ , but both of them will be weak because there will be two electrons at each of two corners (rule 6). These two bonds are the only two spare positive ones, each of the others has one of its electrons already shared with another chlorine atom. In this case the nucleus of the phosphorus atom will not revolve since two electrons are supplied by the two extra chlorine atoms.

Holroyd (*Chemistry and Industry Review*, 1923, XLII., 348) suggests that phosphorus penta chloride should be constituted in an analogous fashion to ammonium chloride and should be an electrolyte: he proposes to carry out experiments to verify this, and should his surmise prove correct,  $\text{PCl}_5$  will be represented by Fig. 21.

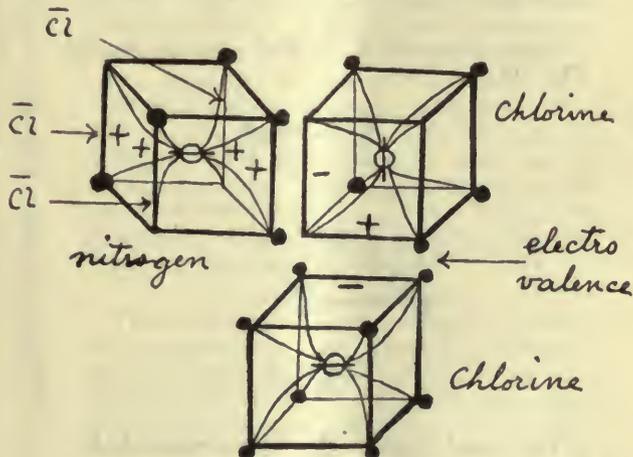


Fig. 21.

It will be interesting to see which formula the results of these experiments will substantiate.

Hydroxylamine will have the constitution shown in Fig. 22.

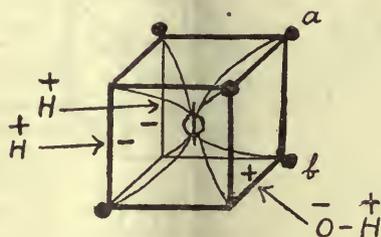


Fig. 22.

Rule 2 makes this an unstable compound: it decomposes at about  $15^\circ$ . According to this formula the hydroxylamates are formed with bases. The oxonium salts will be constituted similarly to the ammonium salts, but with the OH group still attached to the nitrogen. The bond  $a-b$  (Fig. 22) will act with acids exactly as that already described for ammonia (Figs. 14 and 15). The oxygen of the OH group may form a double bond with the nitrogen and the hydrogen go on to the nitrogen, but this oxygen atom would not come into the bond  $a-b$  (Fig. 22) uniting the group to an acid, so that quadrivalent oxygen does not come into the question.

#### Group VI.

General types,  $H_2O$ ,  $H_2S$ , are shown in Fig. 23.

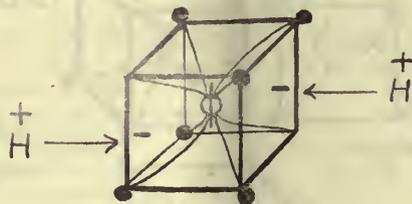


Fig. 23.

$H_2O_2$  and  $H_2S_2$  will be represented by Fig. 24.

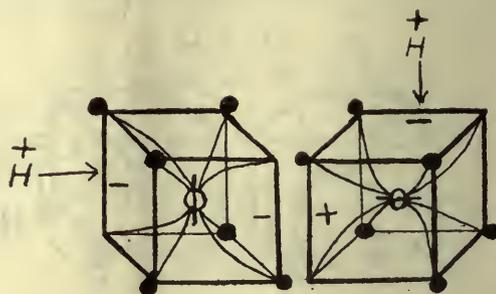


Fig. 24.

In the positive atom, both positive and negative bonds come into play (rules 1 and 2), which accounts for the instability of the molecules. The remainder of the polysulphides of hydrogen may be represented somewhat similarly, and the same may be said for sulphur chloride,  $S_2Cl_2$ , but each chlorine atom will be united to a positive bond in both atoms of sulphur.

#### Group VII.

General types, HF, HCl, etc., see Fig. 1.

#### Group VIII.

General types,  $FeCl_2$ ,  $CoCl_2$ , etc., will have a structure similar to Fig. 4, and types  $FeCl_3$ ,  $CoCl_3$ , etc., similar to Fig. 6.

One difference between these elements and those of groups II. and III. is that these may have varying numbers of electrons in their octets. (See Bury, *J. Amer. Chem. Soc.*, 1921, XLIII., 1602). This fact makes the whole group very complicated: each series of compounds of this group should be worked out separately.

Chemical Research Laboratory,  
School Gardens,  
Shrewsbury.

#### GENERAL NOTES.

The Department of Overseas Trade has issued a *Report on the Economic and Financial Conditions in Germany, to March, 1923*, by J. W. F. Thelwall, Commercial Secretary to H.M. Embassy, Berlin, assisted by C. J. Kavanagh, Commercial Secretary, Occupied Territory, etc.,

Cologne. Pp. 158. Price 4s., or post free 4s. 2½d.

The report contains much valuable information regarding the internal and foreign trade of Germany for the year under review. The conditions prevailing in the various industries are given, and the effect of the continued occupation of the Ruhr is also indicated.

The supplementary statistics occupy 17 appendices.

#### MARKET FOR SURGICAL INSTRUMENTS, NEEDLES, AND RUBBER GOODS IN SPAIN.

Captain U. de B. Charles, Commercial Secretary at Madrid, reports that a demand exists in Spain for surgical instruments, needles and rubber goods, and that the moment is favourable for the introduction of British made articles. German manufacturers have hitherto had a practical monopoly of the trade, but the surtax on depreciated currency, which increases the duty by about 80 per cent., together with the high prices fixed in pesetas, make sales almost impossible, and supplies from Germany are now running short.

Opportunities of entering the Spanish market will be greatly enhanced if correspondence is conducted in Spanish.

The Department of Overseas Trade will supply British firms lists of likely importers and dealers in these articles.

The following headings of the Spanish Customs Tariff relating to surgical articles are quoted for information:

Articles of rubber for hygiene, orthopædic or medical purposes, without admixture of other materials—6 pesetas per kilog.

Medical and surgical apparatus and instruments: (1) of metal—10 pesetas per kilog; (2) of other materials—5 pesetas per kilog.

Orthopædic apparatus—3 pesetas per kilog.

The above duties are quoted in gold pesetas. When the amount of duties is tendered in notes of the Bank of Spain or Spanish silver coins, a surcharge is imposed. This varies monthly, and for May is fixed at 25.51 per cent.

#### GERMANY'S TRADE AND INDUSTRY IN APRIL.

Mr. H. N. Sturrock, the Commercial Secretary at Berlin, has forwarded to the Dept. of Overseas Trade a report on Ger-

man trade and industry during April.

There has been no important change in the economic situation during April. Business continued quiet in the first half of the month. On the 18th, however, in consequence of the renewed fall of the mark, a small revival of trade took place. On this day the Reichsbank were unable any longer to hold the mark, which had remained stable since the end of January.

In the retail trade, disinclination to buy began gradually to disappear; there was even a lively demand from the 18th to the 20th.

In occupied territory, the French succeeded in increasing the despatch of coal and coke. The quantities transported did not, however, amount to one-sixth of the deliveries under the Reparations programme.

#### MINING.

*Coal.*—The pit-coal production in Upper Silesia proceeded without disturbance, and is estimated at about 760,000 tons. The demand for Upper Silesian large coke continued. The large imports of British coal led to the accumulation of stocks, and any palpable improvement on the coal market cannot be expected until a change in the general situation or an increase in exports takes place. Stagnation also occurred in the Central German brown coal district.

*Potash.*—The unfavourable development of market conditions continued. There was also no improvement in foreign sales of potash products.

The sales of chemical bye-products of the potash industry improved with the rise in foreign bills towards the end of the month. Bye-products obtained by electro-chemical process found a good market during the whole month, particularly abroad.

#### ELECTRO-TECHNICAL INDUSTRY.

In the electro-technical industry a further decline of business activity was recorded. The difficulties in the way of obtaining coal and semi-manufactures owing to the occupation of the Ruhr were overcome, but delivery contracts were delayed by transport difficulties.

#### CHEMICAL INDUSTRY.

The falling off in the demand for chemical preparations and ceramic chemicals, which became noticeable immediately after the unexpected rise of the mark, gave place at the beginning of April to a brief revival. The world's market price has, in part, been reached and, in part, exceeded. In particular, German prices for chemicals are higher than those of America, especially as

that country, unlike Germany, enjoys very favourable Customs treatment, not only by Entente countries, but also by Czecho-Slovakia and Poland. It is, therefore, urgently desired that the export duty for laboratory chemicals and ceramic chemicals be soon still further reduced in view of the enormous foreign competition.

#### GLASS INDUSTRY.

In the sheet glass industry, raw material deliveries were satisfactory. There was scarcely any inland demand, and exports decreased by a third as compared with March, as it was not possible to compete with Belgian and Czecho-Slovak prices. The Export Association of German Sheet Glass Factories have issued new offers, taking into consideration the reduction of the export duty to 1 per cent.

In the hollow glass industry the supply of raw materials and coal was satisfactory. Owing to the high costs of production inland business fell off considerably. Restrictions of operations occurred on a large scale, and a number of furnaces were put out.

#### LEATHER INDUSTRY.

Only urgent requirements were covered at the beginning of April. Later, as in the case of raw hides and skins, business improved.

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### THE ROYAL SOCIETY.

THURSDAY, MAY 31, 1923.

Papers read:—

E. GRIFFITHS, D.Sc., and G. W. C. KAYE, D.Sc.—*The Measurement of Thermal Conductivity, No. 1.* Communicated by Sir Joseph Petavel, F.R.S.

G. W. C. KAYE, D.Sc., and J. K. ROBERTS.—*The Thermal Conductivities of Metal Crystals. I.: Bismuth.* Communicated by Sir Joseph Petavel, F.R.S.

C. V. DRYSDALE and S. BUTTERWORTH.—*The Distribution of the Magnetic Field and return Current round a Submarine Cable carrying Alternating Current.* Communicated by F. E. Smith, F.R.S.

SIDNEY RUSS, D.Sc.—*The Effect of X-rays of different Wave-Lengths upon some Animal Tissues.* Communicated by Prof. A. W. Porter, F.R.S.

Papers read in title only:—

E. F. ARMSTRONG, F.R.S., and T. P. HILDITCH, D.Sc.—*A Study of Catalytic Actions at Solid Surfaces. Part XI.: The Action of Alumina and certain other Oxides in promoting the Activity of Nickel Catalyst.*

N. K. ADAM.—*The Structure of Thin Films. Part IV.: Benzene Derivatives. A Condition of Stability in Monomolecular Films.* Communicated by W. B. Hardy, Sec. R.S.

N. K. ADAM.—*The Structure of Thin Films. Part V.* Communicated by W. B. Hardy, Sec. R.S.

W. B. RIMMER.—*The Spectrum of Ammonia.* Communicated by Prof. A. Fowler, F.R.S.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

The Friday evening discourse on June 1, at 9 o'clock, will be delivered by PROF. H. A. LORENTZ, Hon. F.R.S., Hon. M.R.I., Haarlem University. The subject is *The Radiation of Light.*

On Thursday, May 31, SIR WILLIAM M. BAYLISS, LL.D., D.Sc., F.R.S., gave his first lecture on *The Nature of Enzyme Action.*

On Saturday, June 2, ARTHUR W. HILL, Sc.D., F.R.S., Director, Royal Botanic Gardens, Kew, will lecture on *The Vegetation of the Andes.*

On Friday evening, June 15, SIR ERNEST RUTHERFORD will give his postponed discourse on *Life History of an Alpha Particle of Radium*, and his concluding lecture on *Atomic Projectiles* on Saturday afternoon, June 16.

#### PHYSICAL SOCIETY OF LONDON.

A meeting was held on Friday, May 25, at the Imperial College of Science, South Kensington, S.W.

The following papers were read:—

*The Effect of Torsion on the Thermal and Electrical Conductivities of Metals*, by PROF. C. H. LEES, D.Sc., F.R.S., and J. E. CALTHROP, B.A., B.Sc.

*The Use of the Wien Bridge for the Measurement of the Losses in Dielectrics at High Voltages, with Special Reference to Electric Cables*, by A. ROSEN, B.Sc., A.M.I.E.E.

A Demonstration of an "Experiment on the Production of an Intermittent Pressure by Boiling Water" was shown by C. R. Darling, F.I.C., F.Inst.P.

A Demonstration of "A Novel Instrument for Recording Wireless Signals" was given by N. W. McLachlan, D.Sc., M.I.E.E.

PROCEEDINGS AT THE MEETING HELD ON MAY 11, 1923, AT THE IMPERIAL COLLEGE OF SCIENCE, ALEXANDER RUSSELL, M.A., D.Sc., IN THE CHAIR,

*The Duddell Medal.*

Sir William Bragg, F.R.S., Chairman of the Duddell Memorial Committee, handed over to the President of the Physical Society a copy of the Memorial Medal, together with the dies and a certificate for the unexpended balance of the memorial fund. In the course of his remarks Sir William Bragg said that the committee had been formed in response to a widely felt wish that the work of this distinguished scientist should be commemorated in a suitable manner. A sum of no less than £700 had been subscribed, thanks in the main to the energy of Mr. R. S. Whipple, secretary to the committee. As regards the design of the medal, very great pains had been taken to ensure that it should be worthy of the memory of the dead and of the art of the nation to which he belonged. The work had been entrusted to Mrs. Mary Gillick, and the committee felt that their choice had been very fully justified by the result. Mrs. Gillick had devoted immense trouble and care to her task, and the medal she had produced was one of which the Society might be proud.

Photographic slides of the medal were exhibited. On the obverse is a miniature of Mr. Duddell; and on the reverse a figure

symbolical of Science examining the world as she finds it, with legends "The Physical Society of London" and "*Rerum Naturam Expandere*."

Dr. Alexander Russell, President, in accepting the medal on behalf of the Society, said that he did so with gratitude to all who had combined to make this memorial possible, and particularly to Sir William Bragg and Mr. R. S. Whipple, whose initiative had set the undertaking on foot, while their perseverance had carried it to such a successful issue. He had been associated with Mr. Duddell at the City and Guilds Technical College and in other connections. He had always marvelled at the encyclopædic character of Mr. Duddell's technical knowledge, which, coupled with his mechanical skill and inventive ingenuity, had enabled him to make so many contributions of permanent importance to the progress of science and of industry. He had been Treasurer, Member of Council, and Vice-President of the Physical Society, and President of the Institute of Electrical Engineers.

Sir Richard Glazebrook said that it gave him great pleasure to express his warm and intense admiration for Mr. Duddell. The latter had been a cordial helper of the National Physical Laboratory, especially during the war, and had always been ready to give generously from his great store of knowledge and of scientific resource. His memory would be kept alive not only by his own work, but by the admirable medal which had been designed; and it was to be hoped that the latter would encourage others to follow his example and to engage in the field of scientific enterprise in which Duddell had been such a prominent worker.

TERMS OF AWARDS OF THE DUDDPELL MEDAL.

The following resolution was adopted by the Council on May 11, 1923:—

*Duddell Memorial Medal.*

*Resolution.*—That the £400 War Loan 5 per cent. 1929/47 Inscribed Stock be accepted in trust from the Duddell Memorial Fund Committee, and that the income therefrom be expended in accordance with the following regulation:—

A bronze medal shall be awarded by the Council not more frequently than once a year to persons who have contributed to the advancement of knowledge by the invention or design of scientific instruments or by the discovery of materials used in their

construction. The award shall be made without restriction as to nationality or Fellowship of the Society. A parchment Certificate of Award and a sum of money may accompany the medal.

Should more than one person be connected with the invention or discovery for which the award is made, the Council may, at its discretion, present more than one medal and apportion the money accordingly.

The terms of awards shall not be varied except by Special Resolution passed by the Society at a General Meeting and confirmed at a subsequent meeting.

The Eighth Guthrie Lecture was delivered by J. H. JEANS, D.Sc., LL.D., F.R.S., who took as his subject *The Present Position of the Radiation Problem*.

Since about 1900 it has been obvious that classical dynamics are in conflict with experience in certain respects, and particularly with respect to the radiation problem. The observed discrepancies suggest that the laws of nature must in some way be discontinuous. To explain the observed nature of black-body radiation Planck propounded the quantum theory; in the hands of Bohr it soon became apparent that the quantum theory contained also the clue to the line spectrum. Hence arose hopes of rapid development which should explain the whole of the radiation problem and reduce molecular physics to order. Progress, however, has been slow and difficult, and what progress there has been is concerned with the structure of matter and not with radiation.

Einstein's hypothesis of light quanta appeared to possess obvious advantages, but has had to give way before the destructive criticism of Lorentz and others, and the direct experimental test of G. I. Taylor.

The different methods of interchange of energy between matter and ether or radiation may be classified as sub-atomic, atomic, and mass transfers. Typical of the first is the emission or absorption of radiation by a Bohr atom; of the second the motion constituting heat in a solid; and of the third the transmission of momentum occurring when a beam of radiation falls upon the surface of a perfect reflector. An examination of these leads to a consistent view, namely, that physical and chemical transfers take place by quanta, while mechanical transfers take place according to the classical laws.

As an example of the application of general principles to a special problem, the

case of the exchange of energy between a free electron  $e$  and a field of radiation  $X$  may be considered. It appears probable that in such a field the mechanical force on the electron is not represented by the expression  $eX$ . The interchange of energy cannot be covered by the classical laws; neither can it take place by quanta. It thus seems probable that no exchange of energy at all can occur between a free electron and a field of radiation. A conception in regard to this which was used by Einstein in 1917 appears difficult to interpret except on the view that electric forces are a manifestation of a sub-universe more fine-grained than anything we have yet imagined. Many possibilities must be explored before we are driven to believe in a sub-universe of this kind.

#### DISCUSSION.

Sir Oliver Lodge said he shared the enthusiastic admiration which the audience had manifested for the lecturer's work. He would seize the opportunity of asking him one or two questions, and particularly, how he would define the temperature of radiation in a vacuum. As regards the stability of the orbits in an atom, how would Dr. Jeans view the suggestion that circular orbits, which are free from tangential acceleration, are stable; and that when disturbed an electron spirals down to a successive circular orbit, radiation taking place since now the *speed* is varying? Such a change would be of finite duration, not instantaneous.

Dr. Jeans replied that by the temperature of radiation in a vacuum he meant the temperature of matter which could be in equilibrium with space containing that radiation. The word *stability* denoted a conception that had been left behind by the quantum theory, which only thinks of *states*. The notion of asymptotic spirals seems open to the fatal objection that each circular orbit must be quitted determinately for the nearest orbit, whereas in reality each orbit may be quitted for any one of a number of possible orbits. The passage from orbit to orbit may be supposed to occupy a time equal to some 1,000,000 light periods.

A hearty vote of thanks to the lecturer was moved by Dr. C. Chree, seconded by the Lord Rayleigh, and carried by acclamation.



### THE OPTICAL SOCIETY.

A meeting of the Optical Society was held at the Imperial College, Imperial Institute Road, on Thursday, 24 May, when the sixth of the series of lectures dealing with the evolution and development of optical instruments was delivered. It was entitled: *Telescopes before the early part of the Nineteenth Century*, and the lecturer was MR. DAVID BAXANDALL, A.R.C.S.

It was illustrated by exhibits from the collection in the Science Museum.

### THE INSTITUTION OF MINING ENGINEERS.

NOTICE AND AGENDA-PROGRAMME OF GENERAL MEETING, AT GLASGOW, ON JUNE 12TH, 13TH, AND 14TH, 1923.

As previously announced, the seventy-ninth general meeting of the Institution of Mining Engineers will be held at Glasgow, by invitation of the President and Council of the Mining Institute of Scotland, on Tuesday, Wednesday, and Thursday, June 12th, 13th, and 14th, 1923.

#### TUESDAY, JUNE 12.

General meeting at the Royal Technical College, George Street, Glasgow, by kind permission of the Board of Governors.

The following papers will be read (or taken as read) and submitted for discussion:—

*Coal-dust as an Explosive Agent* (with special reference to the experimental work of the United States Bureau of Mines), by GEORGE S. RICE.

*Summary of Research Work carried out for the Committee on "The Control of Atmospheric Conditions in Hot and Deep Mines."*

*The Recent Search for Oil in Great Britain*, by H. P. GIFFARD, M.A., B.Sc.

*A Volcano in the Bathgate Coalfield of West Lothian*, by H. M. CADELL, B.Sc., F.R.S.E.

*The Hurler Sequence in Renfrewshire and Dumbartonshire, and the Evidence of the Basin Structure in the Coalfields of Scotland*, by DAVID FERGUSON.

Excursions, to which ladies are also invited, to the Royal Technical College, Messrs. Mavor & Coulson's Works, and the collieries of the Fife Coal Co., have also been arranged.

### THE INSTITUTION OF ELECTRICAL ENGINEERS.

A Wireless Section meeting will be held on Wednesday, June 6, when a lecture entitled *Wireless Direction-Finding in Steel Ships* will be given by C. E. HORTON.

### ROYAL SOCIETY OF ARTS.

On Friday, June 1, at 4.30 p.m., there will be a lecture before the Indian Section, entitled *The Participation of India and Burma in the British Empire Exhibition, 1924*, by AUSTIN KENDALL, I.C.S., retd., Secretary, Indian Advisory Committee. Sir Charles Campbell McLeod, Member, Board of the British Empire Exhibition, will preside.

### THE FARADAY SOCIETY.

#### THE ELECTRONIC THEORY OF VALENCY.

A general discussion on the above subject is being arranged by the Faraday Society, to be held at Cambridge on July 13th and 14th next. Prof. G. N. Lewis will open the proceedings on the Friday afternoon with a general Introductory Address, and he will probably be followed by Mr. R. H. Fowler, who will contribute a paper intended to open discussion on the physical and inorganic side of the subject. Among those expected to speak are Sir J. J. Thomson, who will be in the chair, Sir Ernest Rutherford, Sir Wm. Bragg, and Prof. W. L. Bragg. The Saturday morning session will be devoted chiefly to applications of the theory in organic chemistry. Sir Robert Robertson, President of the Society, will preside, and opening papers will be given by Prof. T. M. Lowry and Dr. N. V. Sidgwick. Among those expected to speak are Prof. W. A. Noyes, Sir Wm. Pope, Prof. A. Lapworth, Prof. I. N. Heilbron, Dr. W. H. Mills, Prof. J. F. Thorpe, and Prof. R. Robinson. On the Friday evening a complimentary dinner will be given to Profs. Lewis and Noyes and other guests, at Trinity Hall. Arrangements are being made to accommodate those attending the meeting in one or other of the colleges, and it will be possible to include a limited number of non-members of the Society. Particulars may be had from the Secretary of the Faraday Society, 10, Essex Street, London, W.C.2.

## THE FARADAY SOCIETY.

GENERAL DISCUSSION ON THE PHYSICAL CHEMISTRY OF THE PHOTOGRAPHIC PROCESS. At the meetings on May 28.

*The Physical Chemistry of the Vehicle and of the Emulsion*, by T. SLATER PRICE, O.B.E., D.Sc., F.I.C.

Of the substances which were early used in making photographic emulsions, gelatin and the silver haloids are still those which give the best results. Even at the present day we do not know what causes the sensitivity of an emulsion, or if the manufacturer has obtained this information, he has not published it. If the same gelatin is sent to two different firms, the one may reject it as unsuitable whilst the other is just as likely to say that it is eminently satisfactory. One cannot deduce from this that if the acceptance or rejection is based on tests other than the making of an emulsion, the two firms have come to different conclusions as to the causes of sensitivity, since the methods used in making emulsions vary considerably.

In discussing the properties of gelatin it may be of advantage to contrast them with those of collodion, the other medium largely used for photographic emulsions. Collodion differs from gelatin in that it is insoluble in water, a mixture of alcohol and ether being generally used as the solvent. This fact at once limits its applicability. The influence of temperature on the viscosity is also very different with gelatin and collodion. Gelatin sols have the advantage that at the temperatures at which emulsions are made they are quite fluid, whereas at lower temperatures their viscosity increases enormously and at ordinary temperatures they set to a stiff gel, no evaporation of the solvent being necessary before setting takes place. Because of this, as soon as an emulsion has been made, it can be "set" quite readily. In addition to this influence of the hydron concentration there is also the effect of the degradation products which are always present in gelatin. Hitherto no suitable method has been devised of estimating the amount and effect of these degradation products, but it may be mentioned that considerable progress has been made towards obtaining a gelatin which may be classed as a unitary product.

The readiness with which a gelatin gel swells in water is an important factor, both in the preparation of the emulsion and in

development and fixing. Swelling is very sensitive to the influence of various salts, and especially to that of acid or alkali. During the manufacture the "set" emulsion is shredded and washed to remove soluble salts; the washing is generally done with tap or with spring water, both of which contain calcium and magnesium salts, which repress swelling, and consequently the gel does not increase in volume to undesirable proportions. If distilled water were used, it would not only be very costly, but also the emulsion would swell so considerably that not only would the characteristics of the emulsion produced be altered, but the succeeding operations would have to be modified.

As compared with collodion, the dried film of gelatin, as found on photographic plates or papers, offers many advantages. When a collodion film dries there is a tendency for it to become horny on the surface, and since it is insoluble in water hindrance is thereby offered to the penetration of developing and fixing solutions. The gelatin film, however, readily swells in the developer solution, which then diffuses into it almost as readily as it would do into pure water, and hence reaction with the silver haloid readily takes place. Since the gelatin is attached to a rigid support it does not swell equally in all directions, effective swelling takes place only in a direction normal to the surface. The amount of swelling will, of course, depend on the salts, etc., present in the developer solution and also on the temperature. Solutions of the ordinary developers are alkaline, and alkalinity increases the swelling of gelatin to such an extent that very undesirable results would accrue were no other substances present to check the swelling. Carbonates and sulphites are present, however, and when present in concentrations greater than 5 per cent. they depress the swelling in the alkaline solution to a value below that which obtains in water. The depressing effect increases rapidly with the concentrations of the salts, a fact which is taken advantage of in preparing developing solutions for use at high temperatures, as in the tropics.

Another method of preventing the swelling which takes place at the high temperatures of the tropics, is to harden the film before development. This may be done, for example, by the use of a formaldehyde solution containing a salt such as sodium citrate, sodium sulphate, sodium phosphate,

Another factor which is influenced by the swelling is the time of fixation. The more swollen the gelatin the more readily does the thiosulphate diffuse into it; also the greater the concentration of the thiosulphate the quicker will be its solvent action on the silver haloid. Increase in concentration of the thiosulphate tends, however, to decrease the swelling of the gelatin, and there will come a point when this decrease more than counterbalances the influence of mass action. There will thus be a minimum time of fixation, and this is at a concentration of about 40 per cent. thiosulphate; above and below this concentration, the time of fixation increases.

Swelling also has an influence on the washing of the fixed negative (*cf.* recent papers of Hickman and Sheppard). Affecting both the washing and the fixing of the negative is the use of hardening agents, such as potash alum, formaldehyde, etc., in that these have an anti-swelling effect.

Another advantage of gelatin over collodion is that it permits the growth and ripening of crystals. Since the highly sensitive emulsions contain large-sized crystals, it has often been assumed that ripening consists in the growth of large crystals at the expense of smaller ones, according to the Ostwald principle. This is not necessarily the case, since a high-speed emulsion is prepared in a different way from a low-speed emulsion. The increase in size may only be a concomitant factor to the one which produces speed in the grain, that is to say, in the methods used for producing high sensitivity it so happens that increase in size of the grain takes place at the same time as production of speed.

As to what it is which makes gelatin so valuable as a sensitising material, we are still in the dark.

*The Solubility of Silver Bromide in Ammonium-Bromide and Gelatin*, by CHR. WINTHER, COPENHAGEN.

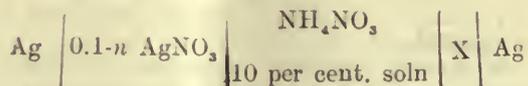
In some theories of the latent image and development it is assumed that the silver bromide grain of the plate is more soluble in potassium bromide solutions, and especially gelatin, than in pure water. These assertions may not hold for very dilute solutions of potassium bromide, since according to the law of mass action, the silver bromide must be less soluble in the said solutions than in pure water. In concentrated solutions there is the possibility of com-

plex ions being formed, the solubility of silver bromide then being increased in proportion to the concentration of these ions. From Hellwig's measurements the complex ion must have the composition  $\text{AgBr}^{-6}$ , the complexity constant being equal to  $1.2 \times 10^6$ .

I have measured the solubility of silver bromide in solutions of ammonium bromide and of gelatin. In some of the experiments I added known quantities of ammonia, ammonium iodide, ammonium chloride and erythrosine.

#### Experiments.

The investigation was made by measuring the electromotive force of a series of elements of the type:—



where X is a mixture of silver bromide, and of that solution, in which its solubility has to be measured. For each solution two identical elements were measured. The potential  $\pi$  very soon attained a constant value, which remained unaltered for many hours.

The experiments showed that the law of mass action is valid for an excess of bromide of between the limits of concentration used. With one exception, the solubility product obtained had the same value. This was also the case when gelatin, and small amounts of ammonia, erythrosine, ammonium iodide and ammonium chloride were added, using concentrations of these substances of the same order as employed in emulsion making.

When both the ammonium iodide and the ammonium chloride are reckoned as bromide, we get the solubility products which are seen to be of the same magnitude as in the other series.

Thus, the solubility of silver bromide in water is not altered by the addition of gelatin, erythrosine, and small amounts of ammonium iodide or ammonium chloride. By the addition of bromide, the solubility is decreased in accordance with the law of mass action.

*Notes on the Photographic Chemistry of Gelatin*, by S. E. SHEPPARD, F. A. ELLIOTT and S. S. SWEET.

The properties of gelatin as a protective colloid (largely associated with its viscosity)

are of importance in photographic chemistry—

(a) For the formation of the emulsion as a polydisperse system of silver haloid grains.

(b) For the inhibition of reduction in absence of exposure, and the regulation of reactions of reduction, etc.

(c) In its function as a reversible water swelling hydrogel, permitting free diffusion of crystalloids (salts, etc.).

These functions of gelatin are largely physico-chemical, *i.e.*, they are determined by the equilibrium of the gelatin: water as a function of concentration, temperature, hydrogen ion, etc. There probably are factors in emulsion making which have little or nothing to do with these physico-chemical conditions.

While the physical chemistry of the vehicle has much to do with the *structure* of the *emulsion* as an aggregate of grains of various sizes, shapes, etc., it has very little to do with the *structure* and *sensitivity* of the grains themselves.

*Gelatin Protective Action.*—The general character of colloid protective action, as inhibition of precipitation, coagulation, and crystallisation—in short, aggregation changes, is not clear. Although viscosity plays some part, there is evidence that more specific factors are dominant. In the precipitation of silver haloids in gelatin, it is obviously inviting to connect the protective action with both the polar character of the silver haloid and of the gelatin.

Results with ash-free gelatin were confirmatory. While the direct solutions show some difference in plasticity (slightly lower) from the diluted ones, in all cases their mobility was greater. These differences indicate, like the difference in gold number observed by Sheppard and Elliott under similar conditions, a *structure* in the sol which depends to some extent on its mode of preparation.

For the practice of the photographic process, the physical chemistry of the jelly is important. Some evidence, and considerable argument, has been brought in favour of various theories of gelatin jelly structure.

The "skin" effect might explain this. Cortner finds that if jellies of different initial concentration are dried, then ground up, and swollen in water again, that the swelling limit still appears to depend upon the initial concentration. We have made some experiments on the anisotropy of drying

and swelling of gelatin jellies which bear on this structure problem. Gelatin jellies on rigid supports tend to dry down and swell up normally to the surface. This is not absolute, as shown by stripping, frilling, reticulation troubles. We have tried to compare the relative *contractility* of different gelatins. By *contractility* we mean the relative extent to which a reduction in unit *area* of a drying sheet of gelatin takes place, compared with reduction in *thickness*.

Contraction varies with the origin of the gelatin. The low value for the sizing gelatin, which undoubtedly contained much hydrolysed material, would suggest that this plays a part. *De-ashing* removes the greater part of these. *Persistent* differences exist in gelatins of different origins. That hydrolytic factors do play a part is shown by results with jellies at different initial  $p_H$  adjustment.

*Anisotropy of Swelling.*—Ten per cent. jellies were dried down under identical conditions and stripped from glass. The sheets were then swollen in water, and the *area*, *weight*, and *thickness* measured. The direct measurements of thickness were not very accurate in this case, owing to the weakness of the jellies, but *volumes* were calculated from the *weights*, using the specific gravities corresponding to each stage.

Figures did not show any unequivocal relation between the contractility and the lateral swelling or expansion. The highest relative expansion is actually given by the poorest grade of gelatin. They point to the existence of individual structural differences in gelatins, depending not simply on actual physico-chemical conditions, but on origin and previous history.

While the total volume swelling diminishes as the concentration of formaldehyde is increased, the lateral swelling is only slightly reduced, on a relative basis of 500 per cent. volume increase, the lateral expansion of the formaldehyde treated material appears to be nearly twice that of the untreated, and fairly constant. In these experiments the  $CH_2O$  is based on dry weight of gelatin, and was mixed with the solution before coating and drying.

An equilibrium or limited swelling appears to be essential to the Proctor-Wilson-Loeb theory. Swelling reaches a condition of negligible increase in reasonable times, but all factors which decrease swelling tend to make *limited swelling* more apparent, while conversely those which increase

swelling tend to make the swelling *unlimited*. It is obvious that this makes for difficulty in respect of assertions as to "swelling limits." However, most photographically operative solutions tend to discourage rather than encourage swelling, relative to *water* at the same temperature, so that it is possible to obtain some fairly definite evidence on the rate and limits of swelling in these. In our work we have used two methods, one by *weighing*, the other by measuring the *thickness*. The weighing method is only partially satisfactory for solutions. To find the *volume* of jelly from the *weight* it is necessary to know the composition and specific gravity of the solution which has entered the film, and which may vary with the progress of swelling.

With solutions of moderate concentration there is not a great difference between that absorbed and that remaining, and the increase in volume can be calculated.

*The Mechanism of the Latent Image Formation*, by F. C. TOY, D.Sc., F.INST.P.

The problem of the reactions which take place in a photographic plate on exposure is of primary importance for knowledge of the complete process. A great advance has been made in the last few years, due to the realisation of the fact that the single silver haloid crystal of an emulsion is the fundamental unit, and a complete theory of the photographic process can only be built up on a knowledge of the behaviour of these individual crystals in relation to exposure.

There is something even more fundamental than the grains themselves, *viz.*, the "centres," the points in the grains from which development starts.

The main facts in regard to the localisation and distribution of the centres are:—

1. They are distributed amongst the grains haphazard.

2. On the average they are distributed equally over the surface of spherical grains, and are concentrated mostly on the edges if the grains are flat plates.

The centres from which development commences are the actual points where the grain has been changed, and therefore indicate the actual distribution of the material of the latent image.

There is a controversy as to how these centres are formed. The different views may be summarised as follows:—

1. They are formed in homogeneous

grains entirely by the light which is incident at points on the plate in finite discrete quantities.

2. They are pre-existent in the grains before exposure as chemically different substance, the function of the light being to change their condition in such a way that they become capable of acting as reaction centres.

3. A combination of (1) and (2). Heterogeneous radiation incident on grains containing specially light sensitive points.

The recent work of Whittaker is an indication that the reconciliation of these theories may be accomplished at no great distant date.

*Exposure Theories*, by S. E. SHEPPARD, A. P. H. TRIVELLI, and E. P. WIGHTMAN.

Exposure theories of photographic developability deal with the quantitative growth of developability with exposure, and with the nature of sensitivity of the photographic material. They may also consider the nature of the latent image.

The salient features of early theories were the assumptions (1) of homogeneity and continuity of the sensitive emulsion, (2) of a like condition of the incident radiation, and (3) of the same for the developed image.

The essential characteristics of later views are, (1) the full recognition of the microscopically and submicroscopically disperse character of the emulsion, and (2) the assumptions (a) that the light may be heterogeneous, *i.e.*, radiated and absorbed in discrete quanta, (b) that the grains of the emulsion may be inherently heterogeneous as to their sensitivity, and (c) that (a) and (b) may both have to be taken into account.

*Absorption of Light and Photocatalysis.*

Any formula based on the older theories must be deduced on the further assumption that the rate of change is proportional to the light absorbed by the sensitive material.

Hurter and Driffeld postulated: (1) only the energy absorbed by unchanged silver haloid is effective in producing latent image; (2) the absorption coefficient of the changed silver haloid is the same as that of the unchanged. It is difficult to attribute a physical and chemical meaning to this, and, as shown by Ross, leads to a mathematical contradiction.

Equations for rate of photochemical change allowing for photocatalysis have been developed by Plotnikoff, but are too unrelated to experimental facts to be of much assistance. Before any such mathematical excursions are attempted, there are other possible assumptions which should be examined.

Newer theories recognise the disperse character of the emulsion as fundamental. Thanks to the investigations of Slade and Higson, Svedberg, and others, it is recognised that not only do the grains, although crystals of one system and class, differ in size and shape, but they differ in sensitivity.

A grain, however small the exposure, might have its developability changed, that is, its rate of reduction by a developer increase with exposure. An emulsion of equal-sized, equally sensitive grains, would then still give gradation under differential exposure, within limits. The less exposed grains would, for a given stage of development, give a smaller portion of developed silver than the more exposed.

But from microscopic examination, it appears (1) generally, with normal developers and exposures, that a grain which has started to develop becomes entirely reduced, without reference to the exposure, and (2) that a grain is either wholly developable, or not at all.

These statements require some qualifications, and a more rigorous experimental verification. It has not yet been conclusively shown that the above statements hold for developers of low reduction potentials, although there are indications that not all of the grains are completely developed in the same way as with high reduction potential developers. Again, it appears that as reduction potential is lowered by bromide, the developability is progressively affected, this influence becoming less with increasing exposure.

Not the ultimate size of developed grains is affected by exposure, but the number only.

Sufficient evidence has been brought to show that in many emulsions "clumps" of contiguous grains are formed which develop as a unit when only one grain of the clump is light-affected. At the same time, there are cases of apparent "clumps," not definitely distinguishable from the others, which do not develop as units.

Since, on the quantum radiation theory, a "clump" may act as a "target" of size equal to its projective area, and since it is

not easy to see how a simple nucleus theory of sensitivity, without "quantum radiation," can give the same chance of development to "clumps" as the former theory, the settlement of this disputed point is of great importance to exposure theories. The sensitivity of a clump is that of its most sensitive grain, or, according to Svedberg, to the number per unit area of grain. On the former, it is purely a function of the projective area of the "clump."

Not only does sensitivity of grain increase with area, because of number of nuclei, but also that nucleus sensitivity increases with grain size. This is in agreement with emulsion practice.

Results of treatment with  $\text{CrO}_3$  and other oxidisers also indicate that the alteration of the sensitivity by the desensitising agent is a function of the grain size, *i.e.*, the ratio of percentage developable grains between the treated and the untreated grains is decreased markedly with increasing grain size, the smaller grains apparently being much more affected by the desensitising treatment than the larger grains.

It is possible that the average area of the spots ( $= \omega$ ) increases with grain size and that either (1) the spots become more resistant to the chromic acid treatment with their increase in size, or (2) that sufficient time is not allowed to dissolve the large ones, the rate of solution of all the grains being uniform but slow. The latter is hardly likely, since the time is far longer than is required to dissolve any developed silver image where whole grains had been converted to silver. The greater resistance in the case of (1) might be attributed to the position of the spots on the octahedral faces of the larger flat grain, instead of on the cubical surfaces of the smaller less flat ones.

*The Sensitiveness to Light of Asphalt as Function of its Degree of Dispersion*, by JACQUES ERRERA (Brussels).

The name of asphalt is given to a brown-black inflammable and fusible natural mixture. Niépce showed asphalt is sensitive to light.

By successively dissolving asphalt in boiling alcohol, in ether, and by submitting the residue to the action of chloroform, Kayser isolated three components, which he calls,  $\alpha$ ,  $\beta$  and  $\gamma$  asphalt, to which he assigns different molecular formulæ with a growing percentage of sulphur:  $\text{C}_{32}\text{H}_{40}\text{S}$ ,  $\text{C}_{64}\text{H}_{92}\text{S}$ ,

$C_{32}H_{42}S_2$ .  $\gamma$  Asphalt alone is really sensitive to light.

It appears:

1. That the viscosity of the solution of raw asphalt is much less than that of asphalt after treatment, and that, of the two, the one which is obtained by precipitation (Farquhar process) is the more viscous.

2. The molecular weight of raw asphalt is five times as small as that of Kayser asphalt, the latter being about half that of  $\gamma$  asphalt (Farquhar).

3. Submitted to ultrafiltration, the solution of raw asphalt lets through into the ultrafiltrate a much greater quantity of product than the solution of asphalt when treated.

Modern theories seem to admit in sensitive asphalt the existence of three substances chemically defined as  $\alpha$ ,  $\beta$  and  $\gamma$  asphalt. When studying the question from a colloidal point of view, it would appear more correct to say that asphalt is a "polydispersoid"; the sensitive part is the one which is found in a state of colloidal dispersion. When chemically analysed, this colloidal part proves to be the richest in sulphur, the valences of which being a factor of polymerism. According as their degree of association is greater or smaller we find in asphalt the intermediate stages between molecular and colloidal asphalt. Sunlight seems to have a coagulating action.

Tests of viscosity, molecular weight, dialysis, and sensitiveness to light corroborate this view.

A new process of sensitisation of asphalt was indicated.

*Plate Sensitometry*, by OLAF BLOCH, F.I.C. (Ilford Research Laboratory).

Considerable advance has been made in plate sensitometry since the time of Hurter and Driffield.

The complete analysis of the quality of an emulsion is a matter of some complexity, and certain points which have arisen in the continuous endeavour to make testing methods more accurate and keep them simple seem of sufficient interest to record.

The so-called speed of a plate is deduced from the straight line portion of the characteristic curve of the emulsion; whilst this is of some value there are many cases (portrait emulsions for instance) when the under exposure curve comprises the most useful portion of the functions of the plate.

To be of value, any system must cover

the case of all emulsions and give useful information on contrast giving power, "cut," character of the under exposure portion of the plate curve, nature of the curve in the region of full exposure, behaviour to developers with regard to the production of veil, and some expression giving a reasonable idea of speed. In special cases some knowledge of resolving power and size of grain is also necessary.

*Fog*.—Fog is a variable so far as the image is concerned, since the greater the exposure the higher the local concentration of soluble bromide produced in development, and the less the fog.

*The Gamma Line*.—Fairly good curves can be obtained using the H. and D. sector wheel, but exposures are too widely apart for reliable work with many emulsions. Good curves can be obtained by using a wedge.

The following method gives good results. A stencil plate is cut in black cardboard, having four sets of circular openings, five in each set; these openings are of sufficient diameter to cover the field of the photometer, and so arranged that each exposed circle is well surrounded by unexposed plate. A series of timed exposures is given to the plate placed in the dark slide behind the stencil. For fast plates, exposures are made 350 cms. from a standardised lamp, having a small loop filament in one plane. The exposures all fall within the straight line portion of the plate curve. After exposure the backing is removed, and the glass is so cut that each set of exposures is protected against trouble arising from the developer at the edges of the plate. Development is carefully conducted, the dish being regularly rocked in four directions.

For certain emulsions, the gamma lines for varying times of development intersect above the Log  $E$  axis. With a view to getting further evidence, ten different emulsions (made by five different manufacturers) were thoroughly tested.

Seven of these had their points of intersection above the Log  $E$  axis and comprised 5 rapid and 2 moderate speed plates. Two had points of intersection on the Log  $E$  axis, and one (a fast panchromatic) had the point below the Log  $E$  axis.

*Temperature*.—An alteration of the development temperature produces a shift in the gamma slope, and a corresponding change in the speed values as deduced from the straight line portion of the curve. The

densities produced at the higher temperature are uniformly greater than those produced at a lower temperature for the same gamma, but in the under exposure curve the same relationship does not hold good.

The light source, the exposure distance and times, the method of making the exposure, the composition of the developer and its temperature, the mode and duration of development, the question of fog, the method and apparatus for measuring density, and the mode of expressing the results, all require discussion and standardisation.

*The Theory of Photographic Dye Mordanting*, by E. R. BULLOCK, B.Sc.

One of the several methods of converting an ordinary photographic image of gray silver into one of a coloured substance consists in first changing the former into an intermediate image possessing a mordanting character and then treating this with a solution of a basic or acid dye. As with all dye mordanting processes, so dye mordanting in photography has not as yet been found to conform to any simple theory.

The mutual flocculation of the respective colloid particles on mixing two colloidal solutions of opposite electrical character was known to Graham. Biltz (1904) enunciated the rule that colloids carrying opposite charges always precipitate each other if mixed in the proper ratio. On mixing solutions of silver nitrate and potassium bromide, precipitation of the silver and bromide ions takes place not only at the point corresponding to the ratio Ag: Br, but also through a small range on either side owing to adsorption. When a silver iodide hydrosol is added to solutions of methyl violet, precipitation occurs over a wide range, but complete mutual precipitation only over a narrow one.

The solubility of silver cyanide in *N* potassium cyanide solution is greater than that of silver iodide in *N* potassium iodide, this than silver chloride in *N* sodium chloride, and this again than silver sulphide in *N* sodium sulphide. As regards the three last-named silver salts, as ordinarily prepared as images in gelatine by precipitation with an excess of the corresponding potassium or sodium salt, this is the order of their decreasing mordanting power for basic dyes. In order to test silver cyanide, a silver image on film was bleached by immersion in a solution of cyanogen; the re-

sulting image of silver cyanide was found to mordant basic dyes, but owing to the abnormal opacity of the silver cyanide image a direct comparison with silver iodide was not feasible. The sulphides of tin, antimony, and arsenic are readily soluble in sodium sulphide, and are excellent mordants for basic dyes. To show this, the silver image is bleached to silver bromide in a ferricyanide-bromide bath, washed, and immersed in a freshly prepared and very dilute solution of a salt of the type of ammonium thio-stannate, etc.

By a series of experiments in which aluminium hydroxide (as an example of a positive colloid mordant) was precipitated in gelatine, and this system then immersed for a sufficient time in solutions of a number of basic and acid dyes, and finally washed in running tap water, it was observed in every case that a basic dye is retained longer by plain gelatine than by gelatine containing aluminium hydroxide than by plain gelatine. The dyes used were acridine orange, brilliant green, capri blue GON, crystal violet O, fuchsine FCOOB, methyl violet, methylene blue B, tannin heliotrope, acid violet 4BS, anthracene blue, complementary red D, Fuchsine S, anthraquinone green, quinoline yellow and tartrazine. On substituting, in a few tests, chrome alum and iron alum for aluminium alum, the same general results were obtained.

The rule of mutual flocculation of colloids of opposite sign is distinctly serviceable as a simple qualitative guiding principle in the study of the subject of the dye mordanting of photographic images.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Specifications Published this Week.*

182084—Soc. Anon des Matieres Colorantes et Produits Chimiques de Saint-Denis, Wahl, A. R., and Lantz, R.—Manufacture of 2-oxyl-aryl-naphthylamines.

196431—Wolvekamp, M. E.—Organic mercury derivatives of aurin tricarboxylic acid and their alkali salts.

*Abstract Published this Week.*

194840—Dyeing cellulose acetate—R. Clavel, Augst, Basle, Switzerland.

Messrs. Rayner & Co. will obtain printed copies of the published specifications, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3295.

## ISOTOPES: RECENT ADVANCES

MADE BY DR. F. W. ASTON.

In the current issue of the *Philosophical Magazine* for May, Dr. Aston records officially further results in the mass spectra work on the chemical elements, and some negative experiments are given which are of interest.

One of the most helpful advances has been the use of more sensitive plates termed *Schumannised plates*, because the treatment of the plate is like that of an ordinary one when the gelatine is removed as far as possible, but in plates used by Dr. Aston the dissolving off of the gelatine, by means of dilute sulphuric acid, is not carried so far.

Dealing now with the elements, etc., given in Dr. Aston's paper, the main points are stated below:—

*Helium*.—At the suggestion of Prof. Mc Lennan, samples of helium from Canadian gas wells were examined for isotopes, but none were observed. In this connection it may be noted that, should there be any  $\text{He}^{++}$  atoms present during analysis, these would register themselves on the plates as if their mass was  $4.00/2$ , which lines could be checked against hydrogen lines of mass 2.016. By this test the decimal difference in mass could be accurately determined, but no  $\text{He}^{++}$  lines could be found, presumably on account of the high ionisation potential of 80 volts which reduces to a negligible figure their percentage numbers in the mixture.

*Nickel*.—Sir. J. J. Thomson had employed nickel carbonyl, but in the quantities then used it decomposed, and the metal was deposited on the walls of the discharge tube. Dr. Aston has overcome this difficulty by diluting the nickel carbonyl with carbon dioxide and regulating the discharge current to a safe limit. The chemically determined atomic weight is 58.68. The isotopes recorded were 58 and 60 in such proportions as to give the atomic weight as a mean figure.

*Metallic chlorides*.—Metallic chlorides are particularly satisfactory to handle in the vapour state owing to their instability.

but these have a violent action on rubber and tap grease. The result, apart from undesirable compounds, is the release of free chlorine. Consequently there is a "perfect maze of lines filling every successive unit place and effectually screening any clear vision of the lines of the element under observation." Moreover, chlorine forms hydrogen addition products, chlorine itself having isotopes, 35 and 37, and for every type of combining particle there will be *two* lines for the monochloride, *three* for the dichloride, and *four* for the trichloride, etc.

*Titanium*.—On account of the foregoing difficulty titanium chloride gave spectra of great complexity and no proper identifications of isotopes could be made. Two promising lines were recorded, but these were identified from previous experiments as being due to tap grease.

*Chromyl chloride*.—This chloride was "even more hopeless, for its action on tap grease and wax was so rapid as to make it quite unworkable."

*Lead ethide and zinc methide*.—No lines were recorded with these compounds, the probable reason being the abundant liberation of carbon and hydrogen compounds from the decomposing ethide or methide. As an instance of the delicacy of the method, a single iodine line 127 appeared when using the vapour of zinc methide, which was supposed to be quite pure, being colourless. Dempster's fine work on the isotopes of zinc is referred to.

*Xenon, krypton, etc.*—This method was successfully used to verify the purity of the xenon from krypton contamination, the sample being one provided by Dr. R. B. Moore, as used in his density determination, thus rendering the density determination free from any criticism on the ground of krypton being present. The value deduced from this determination is 130.2. Dr. Aston considers it a little on the low side, but the mean evaluation in the case of isotopes is not accurate enough to carry weight against a good chemical or density determination. Excellent lines were obtained on the Schumannised plates, and suspected xenon lines 128 and 130 were confirmed.

Dr. Aston here refers to the search for inert gases of higher atomic weight than xenon, and mentions that in this connection two new components of xenon, 124, 126, were discovered.

It will be remembered that Sir J. J. Thomson (*Roy. Soc. Proc.*, 1922, vol. CI., p. 290) found by his positive-ray method two atmospheric constituents of apparent masses 163 and 260, and suggested that these might be due to molecules  $Kr_2$  and  $Xe_2$ .

To make this review up to date and fairly complete, the following abstract from this Journal of May 18, 1923, of Dr. Aston's paper, read before the Royal Society, entitled *A Critical Search for a Heavier Constituent of the Atmosphere by means of the Mass-spectrograph*, is here reproduced:—

"A critical search for a gaseous inert element, heavier than xenon, is described, in which the residues absorbed in charcoal from over 400 tons of air are dealt with.

"The final analysis is made by means of the mass-spectrograph. The result is negative and indicates that such an element certainly does not exist to the extent of 1 part in  $10^{15}$  of air, and probably not to the extent of 1 part in  $2 \times 10^{16}$  parts of air by volume.

"Faint bands observed in the region corresponding to masses 150 and 260 are described and their origin discussed. The first of these is shown to be due to a complex molecule of mercury with a multiple charge, but no conclusion is reached in the case of the other.

"The results of the experiments are not in accordance with the presence of molecular krypton and xenon in the air, recently suggested." See above.

*Tin and the whole-number rule.*—The earlier work on the isotopes of tin is now confirmed, the values being 116, 117, 118, 119, 120, 121?, 122, 124. The intensities of the lines are such as to render it improbable that any of the lines are due to hydrogen addition products except the value 121, this being very faint on the plate.

In this experiment tin tetramethide was used, which was supplied by Sir W. Pope. The evidence that the above lines were due to tin isotopes is supported by the presence of lines 15, 30 and 45 units higher up in the mass scale by reason of compounds  $SnCH_3$ ,  $Sn(CH_3)_2$ , and  $Sn(CH_3)_3$ . These lines show exact whole-number differences, but "when compared with other lines on the plate they give values less than whole numbers by 2 to 3 parts in 1,000." The presence of xenon lines and those of tin monomethide amongst them made it possible to compare the registration of the tin lines with them. If the xenon lines, 134, 136,

represent whole-number masses, then the compound  $Sn^{120}CH_3$  should lie exactly midway if the tin isotope 120 is a whole number, but it is displaced to the left slightly so as to "coalesce partly with  $Xe^{134}$ ," making this line appear broadened.

Dr. Aston remarks as follows: "It seems impossible to imagine any instrumental defect which could give rise to this shift. There appears therefore to be no escape from the conclusion that tin and xenon cannot both obey the whole-number rule. It was realised and emphasised (*Phil. Mag.*, XXXIX., p. 624) that this rule was not to be expected to hold with mathematical exactness owing to the packing effect, but it is very surprising that elements only differing by three units in atomic number should show so large a divergence. It seems probable that the divergence from the mean ( $O=16$ ) is greater in the case of tin than in that of xenon, but since the arithmetic sum of the two (supposing them to be of opposite signs) is only about three times the experimental error, satisfactory settlement of this point will have to be deferred till an instrument of higher precision is available."

*Iron.*—This element gives a volatile carbonyl (prepared by W. H. Mills), and thus makes it possible to obtain a record of this compound on the plate. A strong line was obtained, indicating that an atom of iron existed of mass 56. A fainter line giving a value 54 was also recorded, which may be an isotope, but the line is so weak that iron may be made up entirely of atoms of mass 56, though the chemical atomic weight is 55.84.

*Cadmium.*—Cadmium, though easily vapourised, gives no lines in the expected region. In this experiment a quartz vessel containing the cadmium was lowered into the cathode-ray path by means of a winch. The metal was vapourised and it condensed on the walls of the tube, forming a bright mirror.

It was noted that mercury was completely eliminated from the discharge by the presence of the cadmium, and it did not reappear "so long as the cadmium mirror remained on the walls of the discharge-tube." A method of eliminating mercury is thus discovered.

*Thallium.*—As part of the above experiment, this element was tried without results, and it is probable that the cadmium layer removes the thallium vapour as effectively as it does mercury.

**Selenium.**—The unsuccessful use of selenium hydride (*Phil. Mag.*, XLII., p. 140) led to the volatilising of the element itself with the result that five strong lines were obtained, viz.: 76, 77, 78, 80, 82. There is a faint line at 74. These values were confirmed by a set of corresponding lines 12 units higher up on the mass scale, due to C Se; also lines 28 units higher, due to COSe, were obtained, and some faint lines of CSe<sub>2</sub> were identified. It is to be noted that three selenium isotopes have the same masses as some of those of krypton. This is a case of isobaric heterotopes.

**Tellurium and beryllium.**—Pure tellurium was volatilised, yet no lines were obtained, but this failure is probably due to its high boiling point and consequent low vapour pressure. Tellurium chloride was used without success.

Beryllium acetate was tried, but its immediate decomposition yielding a white oxide prevented this experiment becoming successful. G. P. Thomson's positive ray analysis of this element, however, stands, there being only one value, 9, which is in close agreement with Hönigsmid and Birkenbach's value, 9.018.

**Aluminium.**—The chemical atomic weight of this element is now known to be 26.96, and it is therefore evident that in all probability it is a simple element having only one mass value, 27. Dr. Aston remarks that as a rule odd atomic-weight elements have never more than two isotopes, and the occasional appearance of the line 13.5 is probably due to Al<sup>++</sup> from the electrodes. The line 27 has, however, been observed. Lines 62 and 97, also recorded, indicate mono- and dichlorides of bodies of masses 27 and 28. The latter may be Si<sup>2+</sup> or CO, but the former is probably aluminium, and Dr. Aston says "it is therefore reasonably certain that this element consists mainly of atoms of mass 27, and since there is no evidence of atoms of lighter mass, the chemical atomic weight leads definitely to the conclusion that it is simple."

**Chlorine.**—In the foregoing experiments exceedingly intense lines, 35, 36, 37, 38, have been obtained, but no trace of a line at 39, and Dr. Aston concludes that the hypothetical isotope 39 does not exist.

**Antimony.**—Antimony hydride proved of no use, but antimony methide, prepared by Prof. G. T. Morgan, when introduced with CO<sub>2</sub>, gave values 121 and 123. With sufficient exposure similar lines appear 15 and

30 units higher up on the mass scale due to the mono- and dimethide respectively. Faint companion lines, 122 and 124, appear to be due to hydrides from their irregular intensities. The antimony isotopes seem to be in accord with the whole-number rule. The atomic weight as determined by Willard and McAlpine is 121.77, which agrees with the mean estimate of the above isotopes, judging from the relative intensities of the lines.

#### TABLE OF ISOTOPES.

Dr. Aston gives the table of isotopes as appeared in this Journal March 9, 1923, and he proposes to call the integers *mass-numbers*, as it is evident from the foregoing that there are some cases where the deviation from whole numbers, though small, is still appreciable. The mass numbers are given in the order of the intensity of the mass lines, and numbers in brackets are provisional.

#### SUPPLEMENTARY NOTES.

Those wishing to study the literature exclusively devoted to the non-radioactive isotopes from the experimental (discovery) point of view should consult the following literature:—

Aston: *Nature*—Nov. 27, 1919; Dec. 18, 1919; Mar. 4, 1920; July 1, 1920; Dec. 9, 1920; Mar. 17, 1921; June 23, 1921; Sept. 2, 1922; June 24, 1922; Nov. 18, 1922; Dec. 2, 1922; June 2, 1923.

Aston and Thomson: *Nature*—Feb. 24, 1921.

Aston: *Philosophical Magazine*—April, 1920; May, 1920; Nov., 1920; July, 1921; Sept., 1921; May, 1923.

G. P. Thomson: *Philosophical Magazine*—Nov., 1921.

Dempster: *Science*—April 15, 1921; Dec. 10, 1921.

Dempster: *Physical Review*—Dec., 1921; March, 1922; Dec., 1922.

The basic discovery that stimulated research in connection with isotopes of the non-radioactive class was made by Sir J. J. Thomson when he revealed the duality of neon. See his book, "Rays of Positive Electricity," 1913, or later edition.

The above list may be extended to include experiments made to separate isotopes, their classification, those belonging to the radio-active class, theoretical views, etc.

Announcements of the discoveries appear in *Nature* and *Science*. For fuller accounts see *Philosophical Magazine* and *Physical Review*, as listed above.

## A NOTE ON KAFFIR MELON OIL.

## ANALYSES OF SEEDS.

By Chas. F. Juritz, M.A., D.Sc.,  
F.R.S.E., F.R.S.(S.Af.), F.I.C.

In Science Bulletin No. 6 of the Department of Agriculture, I tabulated thirty-eight analyses of the ring, seed, and pulp of the two well-known varieties of kaffir melon (Tsamma and Monketaan), made, in the latter case, at different stages of ripening, and also gave a brief description of the melons and their adaptability as stock-food. Only one analysis of tsamma seed was made, and in that case the yield of fat or oil from the fresh seed was 4.64 per cent., the corresponding oil-content of fresh monketaan seed ranging (according to eight analyses) from 20.25 per cent. to 23.10 per cent.

The analyses above referred to were shortly summarised by Professor M. Rindl in the course of his article on "Vegetable Oils and Fats" in the December, 1920, issue of the *South African Journal of Industries*.

The tsamma analysed eight years ago had grown in the Vryburg district, and the monketaans in the Cape Peninsula. Early in 1920 I procured, through the Magistrate of Kuruman, supplies of tsamma and monketaan seed from the vicinity of the Kalahari Desert.

These seeds (without further drying) were analysed, with the following results:—

	Tsamma Seed. Per cent.	Monketaan Seed. Per cent.
Water .....	6.57	7.04
Oil .....	12.85	22.10

The oils, which were of a pale-yellow colour, were extracted by means of ether, and showed the following constants:

	Tsamma Seed Oil.	Monketaan Seed Oil.
Specific gravity at 15.5° C. ....	0.917	0.930
Refractive index at 40° C. ....	1.4684	1.4668
Iodine value ....	131.5	118.8
Saponification value .....	161.1	187.9
Acid value .....	1.8	5.8

The iodine value of an oil indicates the amount of oxygen the oil is capable of absorbing from the air, and therefore of drying to a solid elastic film when exposed to the air in thin layers. A good drying vegetable oil usually shows an iodine value between 120 and 200, whereas the iodine value of a semi-drying oil lies between 100 and 120, and that of a non-drying oil between 80 and 100. The monketaan oil examined seems to be near the border line, but the tsamma oil is well within the region of the drying oils. The iodine value of linseed oil, however, is much higher, and varies from 175 to 200. Tsamma oil, in this respect, more nearly resembles sunflower oil (with an iodine value of about 130) and soya bean oil (with a range between 126 and 135).

The saponification value of an oil is an index of the proportion of alkali needed to convert a certain quantity of the oil into soap: hence it indicates the amount of the particular oil which, when treated with alkali, would be required in order to produce a definite quantity of soap. Waxes, which are not capable of yielding soap, have relatively low saponification values, which rarely rise above 140. Lard and tallow, on the other hand, approximate to 200 in their saponification values, while butter-fat exceeds 220. The tsamma oil shows one of the lowest saponification values in the records of vegetable oils, but the monketaan oil is closer to the usual average of this type of oil.

The acid value shows the proportion of free acids in an oil, and is subject to considerable variation in which the age and quality of the oil often play a great part. A high acid value is objectionable in an oil in many ways: if the oil is intended for edible purposes, the presence of much free acid produces a sharp unpleasant flavour; it lowers the oil's potential yield of glycerine; it imparts corrosive qualities to the oil as a lubricant; the free acid tends to cause blocking of oil-ducts by crystallising; and in medicinal and pharmaceutical preparations its action on skin and mucous membrane is of an irritant nature. In neither case quoted above is there any objection against the melon oil.

PROCEEDINGS AND NOTICES OF  
SOCIETIES.

THE ROYAL SOCIETY.

THURSDAY, MAY 31.

Papers read:—

I. GRIFFITHS, D.Sc., and G. W. C. KAYE, D.Sc. *The Measurement of Thermal Conductivity, No. 1.* Communicated by Sir Joseph Petavel, F.R.S.

Among the points dealt with in the paper were the thermal resistance at the bounding faces of a material, the effect of superimposing layers of compressible material, the measurement of the thickness of compressible material, the dependence of the conductivity of timber on structure and moisture-content, the variation of the conductivity of rubber with mineral content.

G. W. C. KAYE, D.Sc., and J. K. ROBERTS, Ph.D. *The Thermal Conductivities of Metal Crystals. I.—Bismuth.* Communicated by Sir Joseph Petavel, F.R.S.

Previously all accurate measurements of the thermal conductivity of metals have been made on bars of heterogeneous structure. It was thought desirable to compare the values so obtained with the more fundamental ones given by single crystals.

A "plate" apparatus has been developed which makes it possible to measure thermal conductivities as high as 0.02 c.g.s. with an accuracy of about 1 per cent., using specimens 2 cms. by 1 cm. in area and about 1 or 2 mm. in thickness.

The thermal conductivities of single crystals of metallic bismuth have been determined in directions parallel and perpendicular to the trigonal axis. The values found at 18° C. are, in c.g.s. units:—

Thermal conductivity of bismuth  
parallel to trigonal axis ... = 0.0159  
Thermal conductivity of bismuth  
perpendicular to trigonal axis = 0.0221  
Ratio of conductivities ... = 1.39

The mean value 0.0191 agrees well with the figure 0.0193 obtained on bars by Jaeger and Diesselhorst in 1899.

This agreement indicates that in the case of bismuth metal in the aggregate, the distribution of the constituent small crystals is random, and that the effect on the thermal conductivity of such inter-crystal-

line layers as may be present is not appreciable. It is hoped to carry out experiments on other metal crystals to see whether this result is generally true.

C. V. DRYSDALE and S. BUTTERWORTH. *The Distribution of the Magnetic Field and Return Current Round a Submarine Cable carrying Alternating Current.* Communicated by F. E. Smith, F.R.S.

PART I. (By C. V. DRYSDALE.)

The experimental results obtained confirm the values of the velocity of propagation and attenuation derived from theory, and the field distribution above the surface agrees very fairly with the theory of Mr. Butterworth derived from consideration of the water as a conducting lamina.

PART II. (By S. BUTTERWORTH.)

Expressions for the distribution of electric force due to a long cable carrying alternating currents and immersed in a sea of uniform depth have been obtained in the form of Fourier integrals. From these integrals formulæ have been developed which cover the following cases:—

- (1) The field above the surface of the sea when the depth of the water is small.
- (2) The field above the sea at large distances from the cable, there being no restriction in regard to depth.
- (3) The field below the surface of the sea for points vertically above the cable.
- (4) The field below the surface of the sea at large distances from the cable when the depth of the sea is great.

SIDNEY RUSS, D.Sc. *The Effect of X-rays of Different Wave-Lengths upon Some Animal Tissues.* Communicated by Prof. A. W. Porter, F.R.S.

The experiments recorded were designed to find whether a differential action exists when X-rays of different wave-lengths act upon animal tissues. Two regions in the X-ray spectrum were selected, and it was arranged that equal doses of X-ray energy were absorbed in their passage through the tissues. It was found that under these circumstances more profound effects were produced by the longer wave-lengths (0.45 to 0.30 A.U.) than by the shorter wave-lengths (about 0.168 A.U.), both upon the normal skin of the rat and upon Jensen's rat sarcoma. The degree of this differential action is more pronounced in the case

of the skin than it is for the tumour, the numerical values being 6 and 2.6 respectively. It is proposed that these numbers be termed "therapeutic factors," and the bearing they have in radio-therapeutics is discussed.

Papers read in title only :—

E. F. ARMSTRONG, F.R.S., and T. P. HILDITCH, D.Sc. *A Study of Catalytic Actions at Solid Surfaces. Part XI.—The Action of Alumina and Certain Other Oxides in Promoting the Activity of Nickel Catalyst.*

In the absence of any carrier for the nickel, the presence of a small proportion (up to 5 per cent.) of an oxide, such as that of aluminium or magnesium, etc., causes considerable increase in the catalytic activity of the reduced metal, the mixed oxides being prepared by precipitation from a solution of the corresponding mixed salts.

When the nickel oxide is deposited on a support, the behaviour is different. Thus kieselguhr, from which the metallic constituents have been extracted, gives a nickel catalyst inferior to that on natural kieselguhr. The activity of the resulting catalyst is restored if alumina to the extent of about 20 per cent. of the nickel is precipitated with the hydroxide of the latter, whereas a proportion of alumina equal to that of the nickel depresses the catalytic activity of the product again. If, however, the latter proportion of alumina is first deposited on the acid-extracted kieselguhr and the nickel hydroxide or carbonate then precipitated on to this preparation, the catalytic activity of the product generally exceeds that of nickel on the natural kieselguhr.

All these observations are explicable on the hypothesis that the action of the non-reducible oxide is mainly mechanical and connected with increase or diminution of the surface area of the exposed nickel.

We have not been able to effect more hydrogenation with a given weight of reduced nickel in presence of these oxides than with the same weight of nickel deposited in the ordinary way on a suitable support offering a maximum of surface, and accordingly we believe that the "promoter" effect observed is simply due to their influence on the available surface of the reduced nickel.

N. K. ADAM. *The Structure of Thin Films. Part IV.—Benzene Derivatives.—A Condition of Stability in Monomolecular Films.* Communicated by W. B. Hardy, Sec. R.S.

1. Derivatives of benzene, such as hexadecyl phenol, containing one long chain and one polar group in the para position, orient on water surfaces like fatty acids, the phenol group forming the head of the molecule in contact with the water. Measurements of the cross-section of the head by the method of Part II. of these papers gave a result in good agreement with the corresponding cross-section of the nuclei of aromatic compounds, deduced from Bragg's measurements on crystals. The relation between the films on water and the monomolecular layer, which would be obtained by repeated cleavage of the crystal, is explained.

2. Films of these compounds show the usual phenomena of expansion to a two-dimensional vapour, described in Part III.

3. Compounds such as cetyl palmitate, palmitic anilide, etc., which contain one polar group placed between two chains or one chain and a ring, do not adhere to a water surface well enough to give measurable condensed films, though in the expanded state such films are often more stable.

4. The para sulphonic acids in hexadecyl and octadecyl benzene give soap-like solutions in water.

N. K. ADAM. *The Structure of Thin Films. Part V.* Communicated by W. B. Hardy, Sec. R.S.

1. Bromine in the  $\alpha$  position in the bromo-acids and esters, increases the cross-section of the molecules in the films. The heads of bromo-acids may pack in several different arrangements, having areas from 32.8 A.U. to 26 A.U.

2. The bromine atom increases the solubility of films of the higher fatty acids. It also lowers the temperature of change from condensed to expanded films; but it does not appreciably affect the properties of the films when expanded.

3. The double linkage in the  $\alpha\beta$  position relative to the  $\text{COOC}_2\text{H}_5$  group increases the cross-section of the molecule in the films, as it does in iso-oleic acid.

4. The transition between two forms of condensed film, such as those found with the substituted areas, seems exactly ana-

logous to that between two polymorphs or allotropic modifications of solid substances.

5. The law found in Part III., giving the increase of the temperature of expansion of the films with increasing length of the hydrocarbon chains, has been confirmed on eight homologous series.

W. B. RIMMER. *The Spectrum of Ammonia*. Communicated by Prof. A. Fowler, F.R.S.

Of the three bands which are associated with the spectrum of ammonia, the ultra-violet band has already been investigated in detail by Fowler and Gregory, and has been found to be represented in the solar spectrum. In the present investigation attention has been specially directed to the "Schuster bands,"  $\lambda$  5635 and  $\lambda$  5670, and the "a band" of Eder and Valenta.

The Schuster bands have given no sign of resolution under high dispersion, and it is probable that they do not occur in the solar spectrum. The a band is of great complexity, consisting of about 3,000 lines, of which many of the brightest have been measured with sufficient accuracy for proper comparison with the solar spectrum; there is, however, no conclusive evidence that this band occurs either in the solar spectrum or in the spectrum of sunspots.

Observations under a variety of experimental conditions are in accordance with previous conclusions that the Schuster bands have their origin in the normal ammonia molecule; while the ultra-violet band is probably due to emission from a more stable combination of nitrogen and hydrogen. In addition, it is concluded that the band is associated with a combination of nitrogen and hydrogen of intermediate stability.

The occurrence of the ultra-violet band alone in the solar spectrum thus indicates that only the most stable combination of nitrogen and hydrogen can exist under the conditions that obtain in the reversing layer.

#### ROYAL SOCIETY OF ARTS.

A lecture was given before the Dominions and Colonies Section, on Tuesday, June 5, entitled *The Economic Conference and the Colonies*, by SIR EDWARD DAVSON. His Grace the Duke of Devonshire, K.G., G.C.M.G., G.C.V.O., P.C., Secretary of State for the Colonies, presided.

#### THE FARADAY SOCIETY.

GENERAL DISCUSSION ON THE PHYSICAL CHEMISTRY OF THE PHOTOGRAPHIC PROCESS.

At the meetings on May 28.

(Continued from Page 352.)

*The Theory of Photography*, by WILDER D. BANCROFT (Cornell University, U.S.A.).

The three fundamental things in photography are Emulsion, Latent Image, and Development. The question of the latent image may be considered as almost settled. I present to-day a theory of development. The theory of the emulsion is still very much up in the air in spite of the work done in the last few years.

#### *The Emulsion.*

The photographic emulsion consists essentially of silver bromide dispersed in gelatine and usually submitted to a ripening process to increase its sensitiveness. Fast plates contain some silver iodide, and slow plates silver chloride. The question of ripening involves what Svedberg called plate-sensitiveness, and was studied by Hurter and Driffeld. Since the conditions of emulsion making are kept secret by the makers, the development of a theory of emulsion making has been slow, and it is extremely probable that present emulsions are nothing like as good as they would have been, had the problem been one which could have been studied by more people.

*Plate Sensitiveness.*—The ripening of an emulsion involves the dissolving and reprecipitation of silver bromide. It has been generally believed that a coarse grain is more sensitive than a fine one, but this is not always necessarily true. At present it is generally admitted that there is no necessary connection between size of grain and speed, although under apparently similar conditions the plate with the coarser grains is usually faster. Sensitiveness is due to differences in structure or composition of silver bromide grains. The smallest grains of the bromide are definitely crystalline and have the same structure as the larger ones, the crystalline form being a cubic lattice. Trivelli and Sheppard have shown that silver bromide crystals belong in the dyakis-dodecahedral class and there is no sufficient reason for assuming the existence at an ordinary temperatures of a stable or metastable bromide.

Ripening is not due to a reduction, to a series of allotropic modifications, or to a coarsening of the grain as such. That eliminates changes in the composition of the silver bromide itself, changes in the chemical state of the silver bromide, and changes in the physical state of the silver bromide alone, which leaves us facing a blank wall if we postulate that the effective grain is pure silver bromide. The only apparent way out of the difficulty is to postulate that the silver bromide grain is a complex of silver bromide, gelatine, and water, and that ripening consists in an unspecified change in the relative proportions of these three. Since this was written, Reinders has shown that silver chloride crystals contain gelatine when they separate from an ammoniacal solution of silver chloride to which gelatine has been added. While it is probable that silver bromide behaves in the same way, this seems to have been assumed rather than to have been shown experimentally. Recent work on catalysis shows that adsorption and catalytic activity vary enormously with the structure of the surface, and perhaps we are dealing with gelatine adsorbed at the surface of silver bromide crystals and not entangled in the space lattice. If the action of the gelatine is solely on the surface, it should be possible to make a fast plate by precipitating silver bromide under suitable conditions from an aqueous solution and emulsifying the crystals in gelatine.

It is possible to obtain a much faster plate with gelatine than with dry collodion.

*Grain Sensitiveness.*—It is admitted that the silver bromide grain is the unit, though the group of grains may act as a single grain. We should thus expect to get the same blackening on prolonged development for widely varying exposures, which is not so. The following hypotheses may be made to account for this:—

1. The incident light may not be homogeneous.
2. The opacity of the silver may vary with the exposure.
3. The grains in an emulsion may vary in sensitiveness.

Silberstein, who starts from Einstein's hypothesis that "light does not consist in a continuous distribution of energy, as in the classical theory, but is entirely split up into light quanta or discrete parcels of very concentrated monochromatic light, each parcel containing a quantum of energy," considers that the bromide grains are bombarded by

light-darts and that a grain is made developable only when the axis of the dart hits it in a point not too near the edge.

The bombardment, without the conception of darts, had been suggested previously by Lowry. But Clark has made attempts to see whether the development of silver haloid grains after treatment with sodium arsenite proceeded in the same way as when light is used, or X-rays, for making the plate developable. Single-layer plates were prepared from a commercial ultra-rapid plate in the manner described by Slade and Higson. The grains in the emulsion were mostly flat plates. The emulsion used was the same as that employed by Toy. The plate obtained as described was examined in the microscope. A few of the grains were observed to be changed completely; but the majority showed centres exactly similar in appearance to those obtained by Toy when exposure is to light. These results indicate that the reduction centres are an essential part of the grain structure, and that they exist in the grains from the time the emulsion is made.

We are forced to conclude, Mees pointed out (in 1915), that grains in an emulsion are of many sizes, and both the sensitiveness and plate curve depend on the distribution of the different sizes of grains. Svedberg showed later that with grains of the same size, the same type of curve is obtained as with grains of assorted sizes. We may look upon each grain as either entirely developable or not developable at all. The behaviour of a haloid grain towards a developer should vary with exposure in a discontinuous way; when the exposure has reached a certain minimum limit the grain becomes developable and remains so until the exposure has reached a maximum limit—solarisation—when the grain suddenly loses its reducibility.

Svedberg (1922) stated that the substance of the latent image in the haloid grain consists of small centres distributed through it or its light-affected part, and these centres are distributed by chance.

Later, Svedberg stated that a statistical study of the distribution of the centres showed that within each size-class of grain they were distributed according to chance.

In the emulsion with nearly spherical grains, of narrow range of sizes, mutual infection occurs little if at all; while in emulsions with a wide range of grain sizes and having many large polyhedral tablets, mutual infection plays a large rôle in deter-



cing the "speed" and the density per unit exposure increment. The result is evidently of capital importance for the theory of sensitivity and exposure; for whether the high correlation of grain size with effective sensitivity is due to a discrete structure of radiation, or to a pre-existing change distribution of sensitising nuclei amongst grains, it is evident that the extension of the definition of grain size to clumps, the existence of mutual infection, is of basic importance for photographic theory.

#### *Latent Image.*

Owing to the very slight change in silver bromide on short exposure, it has always been popular to assume that the latent image is a physical or allotropic modification. Namias assumed polymerisation, Hurter and Driffeld depolymerisation, Bredig mechanical disintegration, Chapman Jones labile form, and Bose a mechanical strain. All these assumptions, and the further one of von Tugolessow that the latent image is an oxidation product, fail, since all the phenomena of the latent image can be duplicated by immersing the plate in a solution of a weak-reducing agent, such as sodium arsenite. This proves that the latent image is a reduction product of silver bromide. It cannot be a single, definite subhaloid because no such compound has been prepared. No satisfactory chemical reactions can be assigned to it, and the prolonged action of light does not yield the pure compound, and this hypothesis cannot be reconciled with the facts of solarisation.

Trivelli at one time postulated the existence of green  $\text{Ag}^2\text{Br}^7$ , blue  $\text{Ag}^3\text{Br}^6$ , yellow  $\text{Ag}^4\text{Br}^5$ , and red  $\text{Ag}^5\text{Br}^4$ ; but he probably does not believe in them now.

The latent image cannot be free metallic silver (nucleus theory), as it does not show the reactions of free silver, and because the hypothesis cannot be reconciled with solarisation.

It is due to silver adsorbed by the bromide because it can be prepared synthetically. It behaves like a phase of continuously varying composition. This hypothesis also accounts for all the chemical reactions of the latent image, and for the facts of solarisation.

#### *The Developer.*

The theory usually held regarding development of the latent image is that the developer is a reducing agent sufficiently powerful to reduce exposed silver bromide

and yet not powerful enough to reduce unexposed silver bromide.

A theory of photographic development must account for the following:

1. A developer must be a fairly strong reducing agent, and yet it is apparently impossible to produce a satisfactory negative with stannous chloride, m-aminophenol, formaldehyde, or gallic acid.

2. There is no appreciable difference between the electromotive forces of unexposed silver bromide and of that which has received a short exposure.

3. All developers develop gelatine free silver bromide readily even though the silver bromide has not been exposed to light.

4. Most developers give negatives after very short exposures and positives after very long ones.

5. Some developers give positives with very short exposures.

6. With any one developer the exposure necessary to cause a change from negative to positive varies with varying concentration of the developer.

7. Very dilute developers act like light and decompose silver bromide without developing it.

8. Some developers work rapidly and others slowly; the difference is not always one of reducing power as measured by electromotive force, though this is unquestionably a factor.

9. Bromide is very effective with some developers and less so with others.

The fact that we get a negative with one developer and a positive with another shows that the potentials of exposed and unexposed silver bromides are not the sole factors. Developers must therefore have other functions than those of reducing agents of varying strengths. The simplest assumption seems to be that we have selective adsorption and thereby markedly varying concentration at the surfaces of the silver bromide grains. If the reducing agent is adsorbed much more strongly by exposed silver bromide than by unexposed silver bromide, the former will develop more rapidly than the latter and we shall get a negative. If the reducing agent is adsorbed more strongly by the unexposed silver bromide than by the exposed silver bromide we shall get a positive. By the adsorption theory we are thus able to predict the possible existence of the three types of fairly strong reducing agents that we actually encounter; but that does not necessarily mean

that the developers really behave in this way. Until some independent proof is furnished, the theory remains an assumption.

In 1913 I discussed the theory of the developer exclusively from the point of view of selective peptisation. I have now laid stress on selective adsorption with selective peptisation as a resultant phenomenon, partly because it seems to me a better way of presenting the subject, but also because Dr. Sheppard tells me that this way of presenting the matter will meet with less opposition from those who know about photography.

*The Most Important Adsorption Reactions in the Photographic Film*, by DR. LUPO-CRAMER (SCHWEINFURT IN BAYERN).  
*Adsorption Phenomena of Silver Haloids.*

Primary consideration should be given to the latent image, but I shall confine my attention to *Optical Sensitising and Desensitising*.

In 1873 Vogel discovered the method of optical sensitisation by means of dye-stuffs, and it is usual to date the invention of orthochromatic photography from that year. But, immediately after the discovery of the Daguerreotype process, phenomena were observed, which undoubtedly depend on a quite analogous sensitisation, described first in 1840 by E. Becquerel on the "action excitatrice, continuatrice et destructive" of light rays. It was observed that the latent image could be made directly visible on a Daguerreotype plate by yellow, green and red light rays, and also that an underexposed image could be intensified by subsequent development in mercury vapour, if the image before development were further exposed under a yellow or red glass. In these cases the colloidal silver formed in the silver iodide by the first exposure is an optical sensitiser. In fact, finely divided silver is like an organic dye; it dyes wool and silk, and can be used exactly like a dye to colour silver haloids, so that Eder, as a result of spectral analytical investigations of photochloride and photobromide gelatin films, which I had prepared, concluded that colloidal silver is an ideal panchromatic sensitiser.

Dyeing of silver haloid by silver and dye-stuffs is in both cases a characteristic absorption process. Shortly after H. W. Vogel's discovery, it was found that silver optically sensitised, but that this was not chloride and silver bromide could be easily

the case with silver iodide, which remained practically indifferent. This is remarkable, since silver iodide can be easily dyed. This tendency for adsorbing dyes, depends less on the chemical nature of this silver haloid than on the fact that silver iodide has a colloidal gel structure, and takes up dye more easily than the bromide or a highly sensitive plate, which from ripening grows into the form of more or less compact large crystals.

Numerous dye-stuffs also act as chemical sensitisers, increasing the total sensitivity towards white light.

The sensitivity of silver bromide is diminished by certain dye-stuffs. It is possible to develop even panchromatic plates in the unscreened light of a candle. Safranines are especially suitable for this, and there I have called it the Safranine Process. Recently E. König and R. Schuloff have introduced the pinakryptols, pinakryptol green being especially good.

Dyeing by desensitisers does not appear to differ from that with sensitisers. Desensitising appears to depend on the oxidising action (by reason of chemical constitution) exerted on nascent silver.

The strongest sensitisers of the cyanine group also act as desensitisers if bromine salts are present to support the tendency of regression of the silver bromide.

It is especially noteworthy that basic dye-stuffs coagulate a mixture of the sols of silver bromide and silver with the formation of photobromide.

#### *Adsorption Phenomena with Silver.*

Both silver sols and also gels resulting from them by coagulation adsorb many substances. The black silver of the photographic negative also shows a strong adsorptive power for many substances, including thiosulphate. If normally developed negatives are hardened with chrome alum before fixation, and then fixed in concentrated bromide, it is possible to obtain the silver free from adsorbed substances. If such a negative is now bathed in thiosulphate, washed, and then the silver dissolved in chromic acid, nitric acid, or persulphate, a residue of silver sulphide remains.

Adsorption of thiosulphate by silver is really the cause of the peculiar reducing action of persulphate. In the lesser exposed parts, the silver is more finely divided than in the high lights, which are more quickly attacked by the persulphate.

## SOCIETY OF GLASS TECHNOLOGY.

The sixty-second meeting of the Society was held in University College, London, on May 16. The President, Prof. W. E. S. Turner, D.Sc., occupied the chair.

At the first session two papers were presented. The first was entitled "*On the Refractive Index Changes in Optical Glass Occasioned by Chilling and Tempering*," by F. TWYMAN, F.Inst.P., and F. SIMEONS, B.Sc., F.Inst.P. Mr. Simeon defined "Chilling" as the rapid cooling from a high temperature, as opposed to the controlled cooling from a medium temperature known as "annealing." Considerable "chilling" could be effected by allowing glass to cool in air from a temperature within or above the annealing range. The process of tempering a metal consisted in the removal of a part of the properties introduced in the preceding operation by heating it to a definite temperature considerably lower than that attained for "chilling," and allowing it to cool slowly. The term "tempering" was applied to the analogous partial recovery of the properties of glass in the annealed state on heating. "Annealing temperature" was defined as the temperature at which internal stresses existing in a glass were reduced to one-twentieth their original amount in 0.26 min.

The effect of chilling dense barium crown and borosilicate crown glasses might be to lower the refractive index by as much as 0.004 and 0.0013 respectively. This lowering was removable by heating to a temperature and for a time which had been ascertained in certain cases. A want of homogeneity could be produced by moulding, owing to surface chilling, which required for its removal a longer maintenance at the high temperature than would suffice to remove elastic stress from a homogeneous sample.

MR. V. STOTT, B.A., F.Inst.P., gave a paper entitled "*Notes on Burettes*," in which he gave details of measurements of the amounts of liquids run from burettes under various conditions. A burette which empties rapidly has a high drainage factor, and the draining from the walls continues over a very long period. In fact, in a 50-c.c. burette emptying in 20 sec., the drainage was not complete in 30 minutes. On the other hand, a burette which has a long emptying time, has a small drainage, which is practically complete after a short time.

Accurate readings can be obtained much more quickly by using a long emptying time and a short drainage than by using a short emptying time and a correspondingly longer drainage time.

The errors occurring through using a burette calibrated for a certain delivery time with a jet which gave different delivery time were dealt with, and in specified instances it was shown that such errors were too large to be negligible.

At the second session the President referred to the death of Sir Albert J. Hobson, one of the first members of the Society. He also intimated that the visit to Paris which had been postponed would take place some time in July.

Two papers were presented. (1) "*A New Method of Glass Melting*," by A. FERGUSON.

This method claimed to melt and refine tank bottle glasses with 30 tons of coal to 100 tons of glass, including a 60 per cent. margin of safety. The process consisted of a cone or column of whirling gases at 1,800° C., into the vortex of which batch ground to a 60-mesh standard was dribbled at the rate of two pounds per second, the carbon dioxide of the limespar and soda having been first driven off in a preheater, so that the work of the furnace was only to raise the temperature from 850° to 1,350°. The particles of finely-divided batch exposed to the heat in a surface which was over 6,000 times that of batch "spread on," and the permeation of the particles was 2,000 times easier. All reactions necessary to form glass molecules took place in a gas at least two million times less viscous than tank metal, so that affinities could reach each other, collide and react millions of times per second, instead of all the energy of the atom being required for hours to find the waiting affinity lurking somewhere in a tank, and when not encountered resulting in seed, striae and unequal strain in the glass. All preheating was done by waste heat after the duty of the heat had been carried out. The coal was retorted, the hydrocarbons saved, air and batch preheated and freed from carbon dioxide (which was later converted into carbon monoxide in the producer). The process was entirely automatic. The batch, instantly melted and refined, flowed through a stream line tank to a periphery gatherer in a fire-hearth.

(2) "Natural Sillimanite as a Glass Refractory," by S. ENGLISH, M.Sc. Results of tests showed that this material possessed properties of value to glass makers. Test pieces were made up by mixing 100 parts of sieved sillimanite with 10 parts of finely-ground clay; such mixture could be made into slabs and pressed into crucibles. These slabs and crucibles were examined for the properties which are the chief causes of trouble to glass makers when using ordinary clay refractories, and the results showed: (I.) The drying and firing shrinkages of the sillimanite mixture were very much less than the corresponding contractions of pot clay mixtures; in fact, when the sillimanite slabs were completely air dried they showed practically no further shrinkage on firing to 1,400°. (II.) The porosity of the fired sillimanite slabs was rather less than the porosity of pot clay slabs fired to the same temperature. (III.) Sillimanite crucibles were attacked much less by molten glass at 1,400-1,420° C. than were similar sized pot clay crucibles. The attack was measured by determining the iron oxide and alumina content of two glasses and remelting each of them for 6 hours at 1,400-1,420° C. in sillimanite and in clay crucibles. The iron oxide and alumina contents were again determined, and comparisons showed that in each case the clay crucibles were attacked three times as rapidly as the sillimanite crucibles.

The Annual Dinner of the Society was held in the Hotel Cecil. The President was in the chair. Among those present were Sir F. W. Dyson, F.R.S., Astronomer Royal and President of the Optical Society; Sir Lawrence Weaver, K.B.E., Director, United Kingdom Exhibits, British Empire Exhibition (1924); H. J. C. Johnston, Esq., President of the Institute of Clayworkers; Frank Wood, C.B.E., B.Sc., and Dr. M. W. Travers, F.R.D., Past-Presidents of the Society; A. R. Upjohn, Esq., I.L.B., Master of the Glaziers Company; R. L. Frink, Director of the Glass Research Association; Mons. Courty, Paris; J. Connolly (Hon. Treasurer); S. English (Hon. Secretary); and others.

The following day a party from the Society had the privilege of visiting the new works of Messrs. James Powell & Sons (Whitefriars), Ltd., at Harrow.

## THE OPTICAL SOCIETY.

### VISIT TO ROYAL OBSERVATORY.

By the courtesy of the Astronomer Royal, a visit has been arranged to the Royal Observatory, Greenwich, on Saturday, June 9, 1923, at 3 p.m. Fellows and Members desirous of availing themselves of the opportunity of visiting the Observatory on this date are requested to send their names to the Honorary (Business) Secretary of the Society at the Imperial College, not later than Thursday, June 7.

### ORDINARY MEETING.

A meeting of the Society will be held at the Imperial College, Imperial Institute Road, South Kensington, at 7.30 p.m., on Thursday, June 14, 1923, when the following papers will be presented and discussed:—

*Levels and level Bubbles*, by S. G. STARLING, A.R.C.Sc., B.Sc., F.INST.P.

*A new form of Balloon Theodolite*, by T. F. CONNOLLY, M.Sc.

*The Primary and Secondary Image Curves formed by a Thin Achromatic Object Glass with the Object Plane at Infinity*, by E. WILFRED TAYLOR.

## THE GEOLOGICAL SOCIETY OF LONDON.

MAY 16, 1923—PROF. W. W. WATTS, Sc.D., F.R.S., VICE-PRESIDENT, IN THE CHAIR.

The following communications were read:—

*The Upper Ordovician Rocks of the South-Western Berwyn Hills*, by WILLIAM BERNARD ROBINSON KING, O.B.E., M.A., F.G.S.

A new species of *Calymene* was incidentally described from the upper part of the Ashgillian, where it is taken as a local index-fossil.

*The Geology of the District around Corris and Aberllefenni (Merioneth)*, by PROF. WILLIAM JOHN PUGH, O.B.E., B.A., F.G.S.

## ROYAL MICROSCOPICAL SOCIETY.

The section of the Society which has been formed to deal with the Industrial Applications of the Microscope, and to assist in the development of Industrial Research in British Industries, held a meeting at 20, Hanover Square, W.1, on Wednesday, May 30.

The demonstrations and exhibits included the following:—

Mr. M. T. Denne, O.B.E., F.R.M.S., demonstrated an improved apparatus for the production of photomicrographs.

Mr. C. A. Newton gave a demonstration of a new form of microscope lamp for easy exchange of paralleliser and polariser.

Mr. Mansell P. Swift demonstrated a Hutchinson universal goniometer.

The following papers were read:—

*On the Microscopical Examination of China Clay*, by Mr. JOSEPH M. COOK.

*The Microscopical Investigation of Sands for various Industrial Purposes*, by Mr. H. B. MILNER.

Professor A. Hutchinson (Pembroke College, Cambridge) presided.

## ROYAL INSTITUTION OF GREAT BRITAIN.

On Thursday, June 7, SIR WILLIAM M. BAYLISS, LL.D., D.Sc., F.R.S., gave his second lecture on *The Nature of Enzyme Action*.

## THE SIXTH INTERNATIONAL MINING EXHIBITION.

TO BE HELD 4TH TO 8TH JUNE, 1923.

Papers to be read at the Oil Conference:

*Monday, June 4.*

*The Riddle of the Carpathians* (Opening Address), by E. H. CUNNINGHAM CRAIG, B.A., F.R.S.E., F.G.S., M.INST.P.T.

*Oil Deposits and the Tectonics of Vertical Pressure*, by DR. MAXMILIAN KRAUS.

*Note on the Genesis of Hydrocarbons and their Localisation in certain zones of the Earth's Crust*, by R. D'ANDRIMONT.

*Tuesday, June 5.*

*Oilfield Waste*, by A. BEEFY THOMPSON, O.B.E., M.I.MECH.E., M.INST.M.M., M.INST.P.T., F.G.S.

*Thursday, June 7.*

*The Mode of appearance of the Petroleum Deposits in the Carpathian Region, with General Consideration on the Genesis of the Petroleum and the source of the Actual Deposits*, by J. VOITESTI, Professor Cluj University.

*An Economic Study of Petroleum Mining by Underground Drainage*, by MAJOR J. A. LAUTIER, M.INST.P.T.

*Friday, June 8.*

*The Standardisation Movement in America and its relation to and application towards the Elimination of Waste in the Petroleum Industry*, by C. A. YOUNG and S. D. TUTHILL.

*The Caribbean Oil Region*, by GEORGE HOWELL, F.G.S., F.R.G.S., M.INST.P.T.

## THE CHEMICAL SOCIETY.

ORDINARY SCIENTIFIC MEETING,

THURSDAY, JUNE 7TH.

The following papers were read:—

Investigations on the dependence of rotatory power on chemical constitution. Part XX. The rational study of optical properties: Refraction a constitutive property.—H. Hunter.

Researches on indium. Part I. Diphenyl indium chloride and phenyl indium oxide.—A. E. Goddard.

The properties of ammonium nitrate. Part VI. The reciprocal salt pair, ammonium nitrate and potassium sulphate.—E. P. Perman and W. J. Howells.

Ring chain tautomerism. Part VI. The mechanism of the keto-cyclol change in the propane series.—E. W. Lanfear and J. F. Thorpe.

The reversibility of additive reactions. Part I. The aldol reaction.—E. H. Usherwood.

Mechanism of the pinacon $\bar{e}$ -pinacolone and Wagner-Merrwein transformations.—C. K. Ingold.

Researches on antimony. Part I. Trim-xyllystibine and its derivatives.—A. E. Goddard.

#### GENERAL NOTES.

##### URUGUAY.

##### TENDERS INVITED FOR GENERAL STORES.

The British Vice-Consul at Montevideo has forwarded particulars of the call for tenders for the supply of general store requirements of the State Electric Light Works of Montevideo.

Tenders in sealed envelopes are to be presented at the head offices of the State Electricity Works Administration before 4 p.m., 12th July.

The list of goods required is extensive, including tools, nuts, bolts, greases, lamp shades, cord, files, saws, lumber, stationery, waste, etc. and firms may tender for all or any part of the requirements.

The full list (in Spanish) and a summarised translation of the general conditions of tender can be consulted by interested U.K. firms on application to the Department of Overseas Trade (Room 84).

The Bulgarian State Railways are desirous of receiving tenders for the supply of linseed oil. A public adjudication of tenders will be held on the 15th June.

U.K. firms who are desirous of receiving further particulars should apply to the Department of Overseas Trade (Reference 10754/F.E./C.C./2).

##### INTERVIEWS WITH THE COMMERCIAL SECRETARY AT COPENHAGEN, DENMARK.

The Commercial Secretary at Copenhagen, Mr. R. M. A. Turner, will be in attendance at the Department of Overseas Trade from the 25th to 30th June, inclusive, and will be pleased to interview, by appointment, United Kingdom manufacturers and merchants interested in export trade to Denmark.

Applications for interviews should be addressed, without delay, to the Department of Overseas Trade, and the reference 7505 F.R. should be quoted.

##### PUBLIC ANALYST FOR GLOUCESTER COUNTY AND CITY.

The Council of the Institute of Chemistry of Great Britain and Ireland advise any Fellow or Associate of the Institute who may contemplate accepting appointment as Public Analyst for the County of Gloucester or for the City of Gloucester on the terms recently advertised to communicate at once with the Registrar of the Institute.

##### CANADIAN CHEMICALS AND ALLIED PRODUCTS, 1919-1920.

A special survey of Canada's chemical industries was undertaken by the Dominion Bureau of Statistics as a section of the Industrial Census to provide a directory of Canadian Chemical Industries and their products for the use of the trade. It also served to assemble data regarding raw materials used, products and by-products manufactured, imports and exports, etc., thus indicating not only the importance of the industry and the progress which it has made in Canada, but also possible new and profitable trade openings in industrial chemical lines.

The present report is the result of the first comprehensive survey of the production of chemicals and allied products in Canada.

Industries are grouped by classes according to the principal component materials of their products; on this principle, the present study was carried out in ten main groups, namely: Coal tar and its products; acids, alkalies, salts and compressed gases; explosives, ammunition, fireworks and matches; fertilisers; medicinal and pharmaceutical preparations; pigments, paints and varnishes; soaps, perfumery, cosmetics and other toilet preparations; inks, dyes and colour compounds; wood distillates and extracts; miscellaneous chemical industries. The industries coming under these items in 1920 comprised 456 establishments, employing more than 17,000 hands. A total of nearly \$120,000,000 was employed as capital, and products aggregating nearly \$122,000,000 in value were made. Pigments, paints and varnishes were easily the leading group. Soaps, perfumery, cosmetics and other toilet preparations came second, with acids, alkalies, salts and compressed gases a close third. Medicinal and pharmaceutical preparations; explosives, ammunition, fireworks and matches; wood dis-

tillates and extracts; fertilisers; inks, dyes and colour compounds; and coal tar and its distillation products followed in the order named.

The continuous advance which represented normal conditions before the war was much accentuated in the last four war years, and it is encouraging to note that during the past two fiscal years the export trade has been maintained at a level very considerably above what the normal pre-war rate of increase would have produced.

Progress in the manufacture of chemicals and allied products in recent years has been rapid and the results attained have more than justified the ventures made. The professional chemist and the chemical manufacturers have combined to advance the common weal, and a feeling of optimism dominates and leads the industry. Opportunities for the development of Canadian chemical industries are being sought out by careful research, and while Canada may not lead the world, there still are some of the chemical industries in which her influence will be strongly felt.

#### CANADIAN CHEMICAL EXPORTS, 1922.

Exports of chemical products from Canada during the past fiscal year amounted to \$14,046,940, as compared with the 1921-22 total of \$9,506,170; and exports of automobiles were more than tripled, shipments of trucks amounting to 3,720, worth \$1,444,549 (1,296, worth \$611,185, in 1921-22); of passenger vehicles 45,108, worth \$25,606,359 (13,428, valued at \$7,421,619, in 1921-22); and of auto parts \$2,355,066, compared with \$1,151,453 last year.

#### PADUA SAMPLE FAIR.

Many foreign countries are to exhibit at the International Sample Fair to take place in Padua (near Venice) in June. This Fair is one of the oldest, if not the oldest, held in Europe.

There is always a good British attendance. Many tourists take the opportunity of visiting this historic town to see the fine array of many categories of products which this event brings together.

The London office of the Italian State Railways & Tourist Department announces that special reduced rate tickets will be issued to Padua during the period of the Fair.

#### NOTICES OF BOOKS.

*The Chemistry of Urea*, by EMIL A. WERNER, M.A., Sc.D., F.I.C. Pp. XII. + 212. London: Longmans, Green & Co., 39, Paternoster, Row, E.C. 1923. Price 14s. net.

The physiological importance of urea in animal metabolism is in itself a sufficient reason for the publication of this volume in the Series of Monographs on Biochemistry under the general editorship of Profs. Plimmer and Hopkins. It will be recalled that urea was the first organic compound to be synthesised without the intervention of "vital force" in 1828 by Wöhler.

In addition, the chemical history of urea is remarkable; this substance, so well-known and thoroughly investigated, has had the erroneous carbamide formula ascribed to it until Prof. Werner's researches became known.

Soon after its discovery and isolation in the latter half of the eighteenth century, it was found to yield  $\text{CO}_2$  and  $\text{NH}_3$  by hydrolysis and by fermentation. This suggested the carbamide structure and received apparent confirmation from the various attempted syntheses of carbamide, which all yielded urea.

The general reactions and decompositions seemed to agree well with this formula and certain anomalous properties and the occurrence of subsidiary products in the syntheses and decompositions were overlooked or ingeniously explained on the basis of the carbamide formula, the acceptance of which has undoubtedly hindered advancement in the study of urea.

During the last decade the author has published a number of scientific communications, giving an account of his own investigations on the chemistry of urea and the results are incorporated—together with much new matter—in the monograph under review.

It is shown that all the syntheses are really similar to Wöhler's, involving the union of  $\text{NH}_3$  with the keto-form of cyanic acid. This is clearly brought out by the author's careful explanation of the mechanism of these syntheses, which have led to his cyclic formula being adopted for this compound.

Further confirmation of this formula is to be found in a study of the reactions of the substance with  $\text{HNO}_2$  and  $\text{NaBrO}$ , although formerly these were regarded as affording proof of the carbamide structure. The

action of hypohalogenites, for example, on urea, was regarded as in complete accord with this, since equal volumes of  $\text{CO}_2$  and  $\text{N}_2$  were evolved. The fact that the volume of  $\text{N}_2$  evolved was decidedly below the theoretical amount was ignored, as was the presence of other gases, *e.g.*,  $\text{CO}$ ,  $\text{N}_2\text{O}$ , and  $\text{O}_2$ .

The author is easily able to reconcile this behaviour with his formula, which also accounts for all the "anomalies" associated with the reactions of urea. In the estimation of urea by means of  $\text{NaBrO}$ , no method is known whereby all the  $\text{N}_2$  can be evolved in one operation, but the author has devised a very satisfactory method involving two simple operations.

The considerable value of this *Monograph* is enhanced by the inclusion of a chapter on *Simple Lecture Experiments* to demonstrate the properties of urea. There are also two useful appendices and a good bibliography and index. J.G.F.D.

*Reports on the Progress of Applied Chemistry*, issued by THE SOCIETY OF CHEMICAL INDUSTRY. Vol. VII. 1922. Pp. 586.

The chemical and technical advances in chemical industry during the past year are recorded in chapters written by leading authorities in the various branches of the subject.

Each section is not merely a summary of the discoveries and inventions for the period under review, but is more in the nature of an authoritative discussion and statement of the recent developments in the industries concerned.

Over twenty technical chemists of repute have contributed to the Reports.

#### • BOOKS RECEIVED.

*Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry for 1922* (Vol. VII.). Pp. 586. 1922. Society of Chemical Industry, 46-7, Finsbury Square, E.C.2.

*Canada, Dominion Bureau of Statistics, Mining, Metallurgical and Chemical Branch. Chemicals and Allied Products, 1919 and 1920.* Pp. 150. 1922. F. A. Acland, Ottawa, Canada.

*Theoretical Chemistry, from the Standpoint of Avagadro's rule and Thermodynamics*, by PROF. WALTER NERNST, PH.D., of the University of Berlin. Pp. XX. + 992. 1923. Messrs. Macmillan & Co., Ltd., St. Martin Street, W.C.2. 28s. net.

#### PUBLICATIONS RECEIVED.

The Ministry of Agriculture and Fisheries leaflet No. 300, *The Breeding and Utility of Pigeons*.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 11900—Cassella & Co. Ges., L.—Manufacture of alkyloxyacridines. May 2.  
 11971—Cassella & Co., Ges., L.—Manufacture of p-dialkylamino arylphosphinous acids. May 3.  
 11849—Damard Lacquer Co., Ltd.—Phenolaldehyde condensation products. May 2.  
 11616—Goldsmid Akt. Ges., T.—Process for refining tin. April 30.  
 12173—Harris, H.—Refining metals. May 5.  
 11617—Imray, O. Y.—Manufacture of vat dyestuffs from anthraquinone. April 30.  
 12017—Johnson & Sons, Manufacturing Chemists, Ltd.—Thermometer stand. May 4.  
 12502—Gray, E. L.—Recovery of caustic alkali used in digesting cellulose, etc. material and simultaneous production of oxalic acid. May 9.  
 12366—New Jersey Zinc Co.—Manufacture of zinc oxide. May 8.  
 12469—Soc. of Chemical Industry in Basle.—Manufacture of dye-stuffs of indigo tint. May 9.

#### Specifications Published this Week.

- 196658—Mehner, H.—Process and furnaces for carrying out chemical reactions and physical processes at high temperatures.  
 196672—King, O.—Amido-phenol compounds.  
 177494—Soc. Chimique de la Grande-Paroisse.—Synthesis of ammonia by means of hyperpressures.  
 191002—Soc. Riard, Allenet et Cie.—Manufacture of butyl chlorides.

#### Abstract Published this Week.

- 194840—Dyeing cellulose acetate—R. Clavel, Augst, Basle, Switzerland.

*Aniline-black and like dyeing.*—Black shades are obtained on cellulose acetate silk, films, &c., by impregnating the material with diphenyl black base and acids, with or without salts or protective colloids, and developing by oxidation. According to examples: acetate silk is impregnated in the cold with a solution containing diphenyl black base, acetic acid, lactic acid, aluminium, chromium, and cupric chlorides, and sodium chlorate, and developed in a drying room at  $80^\circ\text{C}$ .; acetate silk is treated at  $50-60^\circ\text{C}$ . in a bath containing diphenyl black base, acetic acid, and boiled-off liquor, and developed in a bath of ammonium persulphate; or oxidising-agents such as hypochlorite, chloride of lime, persulphate, or perborate, may be added to the exhausted dyebath. Specification 182,830 is referred to.

Messrs. Rayner & Co. will obtain printed copies of the published specifications only, and forward on post free for the price of 1s. 6d. each.



## THE CHEMICAL NEWS,

VOL. CXXVI. No. 3296.

A CHEMICAL BASIS FOR THE  
TREATMENT OF TUBERCULOSIS.

BY LOUISE G. ROBINOVITCH, B.ES.L., M.D.

[A Preliminary Statement of Research  
Work in the Chemical Laboratories of the  
Colorado School of Mines.]

The main part of the tubercle bacillus is generally regarded as consisting of waxy and fatty matter, free fatty acids, and other organic substances. It appears that the waxy coating is the main protection to the bacillus and offers the greatest resistance to chemical attack. If this waxy and fatty matter could be chemically decomposed and destroyed by agents not injurious to living tissue, it seems reasonable to assume that a cure for tuberculosis should lie in such a treatment. This abstract presents a brief outline of the essential features of such a method of attack, developed on the basis of the above assumptions and line of reasoning.

The apparent success of this new treatment depends largely on the agent which I have found to be an effective solvent for the tubercle bacillus. It consists of a highly concentrated, slightly alkaline, glycerol extract of steapsin or lipase, and probably insulin into which has been incorporated a small amount of chloroform. The pure extract of insulin will probably make it possible to use smaller doses of the fat-splitting agent more effectively. Potassium bicarbonate was used to obtain the desired alkalinity. Small doses of bile salts (prepared from ox bile) administered orally increased the effectiveness of the above agent.

An important adjunct to the chemical treatment of the disease is activated oxygen, which acts as does a radio-active ray, by releasing its negative electric charge.

## HELIUM AND ITS USES.

*The following account of helium and its uses is based upon one issued by the British Science Guild, by Prof. J. C. McLellan, F.R.S.*

As is well known, helium is one of the chief constituents of prominences in the

sun which shoot out from this body a distance of many thousand miles, as seen during its total eclipse. In 1868 Sir Norman Lockyer announced the discovery of this element in the sun by spectroscopic observation and named it *helium*. In 1895 Sir Wm. Ramsay obtained helium from a mineral, cleveite, along with argon. Helium occurs in radio-active changes as the alpha particle which is ejected from the disintegrating atom in some cases, and where this type of activity is intense, at a velocity as high as 12,000 miles per second. Sir E. Rutherford has made use of the high velocity of the alpha particle in using it as a projectile for breaking up the nitrogen atom, but the quantities dealt with are infinitesimal.

Of particular interest are the sources from which helium is now obtained. It exists in the atmosphere in the proportion of about four parts to one million of air, by volume; but it exists in much higher percentages in natural gases reaching the present known limit of 1 or 2 per cent. therein in the gas wells situated in the western States of America, particularly in Texas.

In France, some springs yield as much as 5 per cent. It is widely distributed, though in Great Britain the supply is almost negligible, being only one-fifth per cent. in the natural gas at Heathfield, Sussex. At King Spring, Bath, one-sixth per cent. has been found. Canada affords the richest supply so far discovered in the Empire, the localities being Ontario and Alberta, but the percentages are low, being about one-third per cent. of the natural gases. See concluding statement.

Activity in obtaining helium has reached a commercial stage in the United States, where from 30,000 to 40,000 cubic feet of this gas are now being extracted daily, but its export is prohibited by law. Sir Richard Threlfall had suggested in 1915 an inquiry into the helium content of supplies of natural gas within the Empire, and the United States began developing the industry two years after the war.

It is instructive to record that this element was a chemical curiosity immediately prior to 1918, at which time 100 cubic feet would have cost about £300 to collect, and since then nearly three million cubic feet of this gas have been extracted in the United States for use in the American Army and Navy. It is compressed and stored in steel cylinders for use in airships and other purposes.

With regard to its uses, it has just been announced that new airships of the rigid type are approaching completion for the U.S. Government, and that they are being inflated with helium instead of hydrogen, the latter gas being, of course, highly explosive and inflammable. Helium, being non-inflammable and non-explosive, and giving a lifting power of 92 per cent. of that of hydrogen, the desirability of its use in inflating the airship envelopes is made evident. For this purpose hydrogen can be mixed with helium to the extent of 15 per cent. without the mixture being inflammable or explosive in air. As a matter of fact, the engines of airships can be placed within the gas envelope is desired, and a further advantage of helium over hydrogen is that the buoyancy can be increased at will by heating or cooling the gas by electric heaters or other means. Moreover, helium diffuses through the envelope about 30 per cent. less than hydrogen.

It is stated that helium can be used to fill thermionic amplifying valves for use in wireless telephony, and also used as a filler for metal filament lamps and arc lamps.

Prof. Onnes, of Leyden, in 1908, succeeded in liquefying helium having reached a temperature of 490° F. below the freezing point of water, which is within 2 or 3 degrees of the absolute zero. Using liquid helium as a cooling agent, Prof. Onnes found that a number of metals became practically perfect conductors of electricity when cooled down to within a few degrees of absolute zero. An electric current induced in a closed conductor by magnetic induction continued to flow for more than an hour, in this instance the metal being lead. Mercury was also used with a similar result. This is called "super-conductivity," for the metal becomes many million times more conducting at this low temperature than at room temperature.

Under the title, "Need for Development," Prof. McLennan says:—

"From ten to twelve million cubic feet of helium could, however, be obtained annually from natural gases in Canada, and the gas has such direct bearing upon problems of scientific and practical importance that the Governments of Great Britain and Canada might, even from the point of view of national safety, legitimately be asked to follow the example of the United States and operate the plant which was constructed during the late war and was erected and operated for a time at Calgary.

With this plant it was shown that helium of high purity could be produced at less than fivepence a cubic foot. With suggestions received from Prof. Kamerlingh Onnes, of Leyden, and with financial assistance received from the Honorary Advisory Council for Scientific and Industrial Research of Canada, the Carnegie Foundation for Research and the University of Toronto, a magnificent cryogenic equipment has been installed in the Physical Laboratory of the University of Toronto. With its large supplies of liquid air, liquid hydrogen and liquid helium can be obtained. This cryogenic laboratory was opened on January 10 last, and on that occasion demonstrations were given of the production of liquid air, liquid hydrogen, and liquid helium in quantity. It is hoped that the facilities of this laboratory will be used by workers in low temperature research who may find it inconvenient to go to Leyden to work under Prof. Onnes, the distinguished physicist of the Netherlands."

#### ON $\gamma$ RAYS FROM RADIUM D AND RADIUM E.

By Mlle. I. Curie and M. G. Fournier.

A strong preparation of Radium D mixed with some milligrams of lead was employed. The rays were studied and characterised by their absorption in aluminium.

*Method of Procedure.*—The measuring apparatus was a vertical cylinder, of which the upper half contained a gold leaf electroscope and the lower half constituted an ionisation chamber closed by a thin leaf of aluminium 5.5 centimetres in diameter. This apparatus was placed several centimetres above the poles of an electro-magnet giving a field sufficient to completely eliminate the  $\beta$ -rays. The active source was placed in a quartz crucible between the poles at 12 centimetres from the electroscope. The absorbing screens were put very near the leaf which closed the electroscope.

#### MEASUREMENTS AND RESULTS.

The absorption curves were traced as abscissæ.

The examination of the curve obtained shows that the intensity could be expressed:

$$I = I_1 e^{-w_1 m} + I_2 e^{-w_2 m} + I_3 e^{-w_3 m}$$

where  $m$  = mass per square centimetre of the interposed screens;  $I_1, I_2, I_3$ , the initial

intensity of the three rays,  $\omega_1$ ,  $\omega_2$ ,  $\omega_3$ , their coefficients of mass of absorption (often denoted by  $\frac{\mu}{\rho}$ ).

It is necessary to note that the  $\gamma$ -ray of Polonium, whose mass coefficient of absorption was found equal to 230 (indicated by Chadwick and recently confirmed by Mme. Curie) is too much absorbed to intervene in the curves with which we are concerned. After obtaining certain data, the authors proceeded to some chemical operation with a view to separate the Radium D and Radium E.

The mixture was dissolved in hot nitric acid and Radium D, crystallised on cooling after concentration, lead nitrate being insoluble in concentrated cold nitric acid. Radium E, separated in this way is still slightly mixed with lead and Radium D. The polonium was finally separated by deposition on a silver blade.

The absorption curves corresponding to the two portions, Radium D and Radium E, were traced as soon as possible after separation.

The changes shown in the curves by the destruction of Radium D in one portion separated by its reformation into the other were studied at the same time as we followed the evolution of the quantity of Radium E by measuring these  $\beta$ -rays with the aid of an electrometric installation.

A study of the curves obtained shows that the penetrating rays III arise from Radium E.

The results are shown to be in good accord with those of Rutherford and Richardson, who give mass coefficients 16.5 and 0.36 respectively for rays I and II.

The authors have established the existence of penetrating rays III, attributable to Radium E. Their coefficient of absorption has also been determined.—(*Comptes Rendus*, 1923, CLXXVI., 1301-4.)

### IS THERE AN ELEMENT OF ZERO ATOMIC NUMBER?—III.\*

By F. H. LORING.

In pursuance of this study, it is of interest to note that Sir E. Rutherford

(*Bakerian Lecture: Prof. Roy. Soc.*, 1920, Vol. XCVII., p. 398) suggests that it is by no means impossible for an atom of mass 1 to exist with zero nuclear charge. "On present views," quoting from the above lecture, "the neutral hydrogen atom is regarded as a nucleus of unit charge with an electron attached at a distance, and the spectrum of hydrogen is ascribed to the movements of this distant electron. Under some conditions, however, it may be possible for an electron to combine much more closely with the H nucleus (proton), forming a kind of neutral doublet. Such an atom would have very novel properties. Its external field would be practically zero, except very close to the nucleus, and in consequence it should be able to move freely through matter. Its presence would probably be difficult to detect by the spectro-scope, and it may be impossible to contain it in a sealed vessel. On the other hand, it should enter readily the structure of atoms . . ."

Prof. Eddington, in his book, *Mathematical Theory of Relativity*, discusses this problem from the energy or mass side, and he points out that the complete neutralisation of a proton by an electron might give rise to an appreciable loss of mass that would pass out as electromagnetic radiation.

It will be seen that these ideas involve a nuclear atom of zero atomic number; only in the case of complete neutralisation such an element would become more or less massless, if Eddington is correct in his surmise.

In the instance of *complete* neutralisation, it is supposed that the electron and the proton *coalesce*, i.e., that they merge to form one entity if such an entity can preserve its existence as such. Now, Sir J. J. Thomson puts forward the view, which has been under consideration for some time, that when the electron approaches sufficiently near to the positive nucleus, then a repulsion sets in. Sir J. J. Thomson, in the *Journal of the Franklin Institute*, May, 1923, page 597, says:—"I shall assume that the law of force between a positive charge and an electron is expressed by the equation—

$$F = \frac{Ee}{r^2} \left( 1 - \frac{c}{r} \right),$$

where

F=attraction between the charges.

\* See "Chemical News," this volume, pages 307 and 325.

$E$  = the positive charge on the core,

$e$  = the negative charge on the electron,

$r$  = the distance between them,

$c$  = a constant varying from one kind of atom to another; it is the distance at which the force changes from attraction to repulsion and is of the order of  $10^{-8}$  cm.

Sir J. J. Thomson remarks that if the law of force is that just given, "then a number of electrons can be in stable equilibrium round a charge without necessarily describing orbits round it." In this connection, Sir J. J. Thomson calls attention to Ernschaw's theorem: that no stable configuration in which the electrons are at rest or oscillate about stable positions is possible when using only the inverse-square law of distance. Furthermore, an example is given which makes planetary phenomena non-applicable to the atom, for in the case of Saturn's rings, the particles do not repel each other as the electrons do. In this treatment of the problem it is assumed that the ordinary law of attraction applies at considerable distances, but when the distance becomes sub-atomic, so to speak, then the law no longer applies, and this introduces a new law, as indicated above.

The argument in its present development leads again to the improbability of there being an atom, or nuclear magnitude, of zero atomic number, and it is necessary to fall back upon the reasoning of Part II., in which the electron was the only entity that could have a place before hydrogen and its zero atomic number was only acquired by virtue of its neutralising quality, though this property is limited if the views of Sir J. J. Thomson are correct. In short, the electron cannot coalesce with the proton and form a stable system.

We have here a case of scientists of great eminence working out different explanations of phenomena which seem at variance in some fundamental respects.

The subject is of interest, in the writer's opinion, and some further views may be offered.

## A PERIODIC FUNCTION OF ATOMIC WEIGHTS.

By ALEXANDER SAKOSCHANSKY, B.Sc.

There exists in the periodic system, certain groups of elements, which establish a numerical relationship between the elements, and with which atomic weights can be calculated.

The arrangement of the elements, calcium, rubidium, vanadium, cerium, and phosphorus, in the a group of six elements, can be described in the following way: Ca is diagonally adjacent to Rb on its left, and V is separated by an interval of two elements to the right; Ce is vertically adjacent to the element which is diagonally adjacent to the left to V. Phosphorus of the same valency as V is the eighth element from it. The sixth member of the group is bound by the arithmetical-chemical identity:—

$$\frac{\text{Ce}}{\text{V}} \cdot \frac{\text{Ca}}{\text{Rb}} = \frac{4}{\text{P}}$$

In the following group Cl. forms a pair with S in the same way as P and Ar or Ca. Cl. is the seventh element from Cr. The pair of elements on the right-hand side of the equation are adjacent in the periodic system, with the exception of phosphorus. The five groups are tabulated, with intervals and valencies shown.

$$\begin{array}{ccc} \text{III.} & & \text{III.} \\ \frac{\text{Fe}}{\text{Ag}} \cdot \frac{\text{Zr}}{\text{V}} & = & \frac{\text{Sc (5)}}{\text{Ti}} \end{array}$$

$$\begin{array}{ccc} \text{VII.} & & \text{VII.} \\ \frac{\text{Mn}}{\text{Cd}} \cdot \frac{\text{T}}{\text{Ti}} & = & \frac{\text{Cl}}{\text{K (6)}} \end{array}$$

$$\begin{array}{ccc} \text{VI.} & & \text{VI.} \\ \frac{\text{Cr}}{\text{In}} \cdot \frac{\text{Sr}}{\text{Sc}} & = & \frac{\text{S}}{\text{Cl (7)}} \end{array}$$

$$\begin{array}{ccc} & & \\ \frac{\text{Ce}}{\text{U}} \cdot \frac{\text{Ca}}{\text{Rb}} & = & \frac{4}{\text{P (8)}} \end{array}$$

$$\begin{array}{ccc} & & \\ \frac{\text{La}}{\text{Ti}} \cdot \frac{\text{K}}{\text{Kr}} & = & \frac{1}{\text{Al}^2 \text{ (9)}} \end{array}$$

EINSTEIN'S THEORY OF  
RELATIVITY.FURTHER ECLIPSE TEST PHOTOGRAPHS NOT  
NECESSARY.

The examination of the photographs taken during last September's total eclipse of the sun has resulted in a remarkable verification of the curvature of space and the bending of light rays demanded by Einstein's theory of Relativity Gravitation. The American, Canadian and Australian parties submitted the theory to critical test.

The photographs obtained by Prof. Chant, of Toronto, and Dr. Campbell, of the Lick Observatory, have now been carefully measured, and the necessary mathematical computations made, with the result that all the stars shown have been found to be displaced by the exact amount predicted by Einstein. It was proposed to repeat the test next September, at the time of the total eclipse visible in N. America, but Dr. Campbell is so convinced by the results of last year's eclipse, and those of 1919 by Greenwich astronomers in Brazil, that there can now be no possible doubt as to the correctness of the Relativity theory, and that further corroboration, so far as the eclipse test is concerned, is quite unnecessary.

The measurements of the Australian plates have not yet been completed, the task being now in progress at Greenwich, but they are believed to be as conclusive as those taken by the Canadians and Americans. It may now be taken that Relativity has survived two of the three tests to which it can be subjected—those depending on the deflection of light passing near massive bodies in space and the movement of the orbit of the planet Mercury in defiance of Newton's laws. The third test, which involves a change in the position of certain lines in the sun's spectrum, is the most difficult of the three to apply, and no definite result has yet been obtained. But Professor Einstein is confident he will obtain clear evidence of this shift of the solar spectral lines by means of a special apparatus he has had erected at Potsdam Observatory.

There is, however, no likelihood of any more Einstein photographs being taken when the sun is eclipsed. It is a costly work, and prevents astronomers undertaking other eclipse observations.

PROCEEDINGS AND NOTICES OF  
SOCIETIES.

## THE ROYAL SOCIETY.

THURSDAY, JUNE 14.

Papers read:—

C. CHREE, F.R.S. *Magnetic Phenomena in the Region of the South Magnetic Pole.*

O. R. HOWELL. *The Catalytic Decomposition of Sodium Hypochlorite by Cobalt Peroxide.* Communicated by Prof. T. M. Lowry, F.R.S.

NINA M. HOSALI. *The Seismic Waves in a Visco-Elastic Earth.* Communicated by Prof. L. N. G. Filon, F.R.S.

Papers read in title only:—

J. W. LANDON and H. QUINNEY. *Experiments with the Hopkinson Pressure Bar.* Communicated by Sir Alfred Ewing, F.R.S.

S. F. GRACE. *Free Motion of a Sphere in a Rotating Liquid at Right Angles to the Axis of Rotation.* Communicated by G. I. Taylor, F.R.S.

B. F. J. SCHONLAND. *The Passage of Cathode Rays through Matter.* Communicated by Prof. Sir Ernest Rutherford, F.R.S.

THURSDAY, JUNE 7.

Papers read:—

SIR CHARLES SHERRINGTON, P.R.S., and E. G. T. LIDDELL. *Stimulus Rhythm in Reflex Tetanic Contraction.*

K. N. MOSS. *Some Effects of High Air Temperatures and Muscular Exertion upon Colliers.* Communicated by Dr. J. S. Haldane, F.R.S.

Paper read in title only:—

F. A. E. CREW. *The Significance of an Anochondroplasia-like Condition met with in Cattle.* Communicated by Sir Arthur Keith, F.R.S.

The Croonian Lecture will be delivered on June 21, by Dr. F. F. Blackman, F.R.S., on *Plant Respiration as a Catalytic Process*.

### THE FARADAY SOCIETY.

GENERAL DISCUSSION ON THE PHYSICAL CHEMISTRY OF THE PHOTOGRAPHIC PROCESS.

At the meetings on May 28.

(Concluded from Page 362.)

*On the Sensitivity of a Silver Bromide Emulsion*, by WALTER CLARK, M.Sc., A.I.C.

Consideration of some of the older work of Lüppo-Cramer, Reinders, Bancroft and others establishes beyond doubt the heterogeneity of the silver haloid grains of a photographic emulsion. In a purely mathematical or physical investigation of the complex problems of the photographic plate, such a course would probably be a natural one to pursue, as representing the simplest possible case. Since, however, the whole problem of sensitivity seems to be bound up with the presence of traces of material which is not silver haloid, the problem is one which is not capable of solution by the mathematician or the physicist alone. Before the physical laws underlying the photographic process can be completely elucidated it will be necessary for a complete chemical investigation to be carried out in connection with the actual process of emulsion making and the effects of subsequent treatment on the finished plate. The problem will probably involve the application of the laws of heterogeneous equilibria, and of a study of the formation of complexes and of the process of adsorption.

The sensitivity of a fast plate is due primarily to grains of material which is not silver bromide. By removal of the latent light-image with chromic acid solution, the speed of a fast plate is reduced to a certain low minimum. This is a natural consequence of the existence of a limited amount of substance in the grains, to which their high sensitivity is due. It is quite probable that the sensitivity promoting material has of itself little or no sensitivity to light, but that it acts as a sort of photocatalyst by increasing sensitivity.

The reduction of sensitivity of a plate by destruction of the latent light image by chromic acid is much more marked than that brought about by merely bathing a plate in chromic acid without a preliminary exposure. Also the fog resulting from the action of hydrogen-peroxide turpentine vapour, nitric, sulphuric, and hydrochloric acids is eliminated by bathing the plate in a mixture of pina-flavol, alkali bromide and acetic acid.

The product of the action of light (and fogging agents) on the plate is much more readily attacked by chromic acid (and acid-bromide-dye mixtures) than is the sensitivity-giving material itself, although this latter is slowly attacked.

*The Chemistry of the Red Toning of Sulphide-Toned Prints*, by A. and L. LUMIERE and A. SEYEWETZ (Paris). Communicated by A. F. Clerc (Paris).

#### Summary:

Silver images which have been sulphide toned obtain a colour ranging from brown to red chalk in a solution of gold chloride to which has been added a sulphur compound, such as thiourea, thiosinamine, ammonium sulphocyanide, or ammonium thiosulphate.

This toning takes place only with silver sulphide and only on the condition that a sulphur compound is present in the gold toning bath.

The silver sulphide, during the toning process, fixes a very considerable quantity (about 133 per cent. of the weight of the silver) of gold and also a certain proportion of sulphur, somewhat greater than that corresponding with the formation of gold sulphide.

The toned image thus appears to consist of a double sulphide of silver and gold.

*Some Future Problems in Photography*, by J. PLOTNIKOV.

From the standpoint of pure photochemical research the investigation of the properties of the photographic plate is full of difficulties, because the photochemist is interested, before everything, in the investigation of reactions, taking place under simple conditions, where the photochemical properties and laws are most obvious. The photographic plate, however, is the most complicated thing imaginable, the complications being artificially increased in order to obtain various desired technical

effects. For photo-chemical investigations the pure salts of silver should be used, as was done only recently by Schwarz and Stock, Hartung, Koch and du Prel, Fajans, and others; even more desirable would be an investigation of pure solutions of silver salts.

The silver salts are in a state of fine dispersion in the medium (gelatin), which, itself, is colloidal and therefore not homogeneous. The molecular weight of the silver salts under such conditions is unknown, and is apparently dependent on the way in which they are obtained. They form, with the gelatin, complex salts of an unknown structure and probably also of variable composition. The gelatin itself, as a medium, will have an influence, which cannot be strictly defined, on the photo-chemical reaction, and this influence will vary with the source and the mode of preparation of the gelatin. Moreover, the gelatin adsorbs and binds chemically the free halogens. The silver salts also adsorb various impurities, which again may influence the photo-chemical process.

The blackening of the plate is an unknown function of the dispersity and of the granular size of the grains of the silver salts. The extent of the surface of the grains exposed to the influence of light is unknown and variable; also the gelatin acts as a screen. It follows that the conditions of light in such a dull medium cannot be simple, since there is: reflection of light from the outer surface of the gelatin outwards, from the inner surface of the glass into the gelatin, and from the individual grains; mutual covering of the individual grains; scattering of the light and photo-chemical and thermal adsorption of light in the grains themselves and in the medium.

The blackening of the photographic plate is not a true representation of the primary photo-chemical process but a summation effect of all the innumerable and indefinable factors referred to above, which factors are sometimes quite accidental and arbitrary in character. Just as it was in the time of Daguerre, the photographic plate is a work of art, which can be used as an aid in scientific investigations, but cannot be the object of scientific research.

*Nucleus Isolation and Desensitisation*, by DR. LUPPO-CRAMER (Schweinfurt, Bavaria).

Since my first communication I have obtained results which open up new points of

view in the consideration of dye-reactions. One piece of evidence in support of the oxidation theory of desensitisation was, that if an exposed silver bromide plate was bathed in a solution containing a bromide and a desensitising dye, further exposure to light bleached the latent image. At first, sensitising dyes, for example, erythrosin and rhodamine, did not give this reaction, which consequently appeared to me to be due to the desensitising (oxidising) action of the safranines. In a new series of experiments, however, and contrary to expectation, it has been found that some typical sensitisers, for example, ethyleyanine and pinacol in the presence of a bromide and in weakly acid solutions, have a much more destructive action on the latent image than the safranines. Moreover, in the presence of bromide, some sensitisers destroy the latent image to a great extent even in neutral solutions, whereas phenosafranine, for example, has only a slight photographic reducing action even in the presence of bromide. Developers (metol, and even quinol) in the presence of potassium bromide, also reduced photographically the latent image to a greater or lesser extent, whilst in all these cases bromide alone is practically without action. It appears that in all these reactions the bromide is the real oxidising agent, the dyes and developers only facilitating the attack of the oxidiser. In a preliminary way, I have assumed that the dyes, etc., when they are adsorbed by the silver bromide, isolate the exposed nuclei by a kind of adsorption replacement, and thus make possible the attack of even very weak oxidising agents. As is well known, S. E. Sheppard and G. Meyer assume that developers are adsorbed by silver bromide, although I am not in agreement with their view that the accelerating action which iodides have on development can be explained in this way.

I have previously considered the desensitising action of the safranines to be due to their behaviour as oxidising agents, but in the light of the facts just mentioned, the bleaching of the latent image in the presence of potassium bromide can no longer be ascribed to an oxidising action of the dye, and consequently the facts in support of my theory go by the board. This theory however, is not completely overthrown, since all known desensitisers possess weakly oxidising properties.

Strict proofs in favour of or against the oxidation theory of desensitisers are certainly to be desired, but it is scarcely to be expected that a definite decision can be arrived at by means of reactions carried out in a test tube, since it is just their relatively small oxidising power which appears to make the desensitisers suitable for their typical reactions. If the dyes were stronger oxidising agents they would of themselves (without bromide) reduce photographically the latent image, that is, they would be of no practical use.

I give reasons for discarding the chief proofs which I gave originally in support of my oxidation theory, but one must demand of other theories that they are also supported by experimental proof.

#### ROYAL SOCIETY OF ARTS.

The Sir George Birdwood Memorial Lecture, entitled *The Influence of Race on Early Indian Art*, by SIR JOHN H. MARSHALL, C.I.E., M.A., LITT.D., F.S.A., Director-General of Archæology in India, will be delivered on Friday, June 15, 1923, at 4.30 p.m. The Most Honourable the Marquess Curzon of Kedleston, K.G., G.C.S.I., G.C.I.E., P.C., F.R.S., Secretary of State for Foreign Affairs, will preside.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

The Friday evening discourse on June 15, at 9 o'clock, will be delivered by SIR ERNEST RUTHERFORD, LL.D., D.Sc., F.R.S., M.R.I., Prof. of Natural Philosophy. The subject is *The Life History of an Alpha Particle from Radium*.

Afternoon Lecture at 3 o'clock.—On Saturday, June 16, SIR ERNEST RUTHERFORD, LL.D., D.Sc., F.R.S., will give his sixth lecture on *Atomic Projectiles and their Properties*.

A General Meeting of the members of the Royal Institution was held on June 4, the Duke of Northumberland (President) in the chair. It was announced that the Managers had elected Sir William Bragg, Fullerian Professor of Chemistry, Director of the Laboratory, Superintendent of the House, and Director of the Davy Faraday

Research Laboratory. The thanks of the members were returned to Dr. J. J. S. Rowe for his donation of £1 to the fund for experimental research. The Secretary reported the decease of Professor E. W. Morley, an honorary member of the Institution, and a resolution of condolence with the relatives was passed. Mr. G. E. Gask, Mr. John Lister, Mr. P. Ainsworth Means, Mrs. Robert Mond, Mr. F. C. Oldfield, Mr. Edward Talbot Paris, Sir Frederick Rice, Mr. C. M. O. Roving, and Mr. W. S. Rowntree were elected members.

#### THE CHEMICAL SOCIETY.

A lecture was delivered by PROFESSOR CHARLES MOUREU (President of the Société Chimique de France), entitled *Les Gaz Rares des Sources Thermales, des Grisons et Autres Gaz Naturels*, on Thursday, June 14, at 8.30 p.m., in the Society's Rooms, Burlington House.

#### PHYSICAL SOCIETY OF LONDON.

At the meeting held on May 25, Alexander Russell, M.A., D.Sc., in the chair, the following papers were read:—

*The Effect of Torsion on the Thermal and Electrical Conductivities of Metals*, by PROF. C. H. LEES, D.Sc., F.R.S., and J. E. CALTHROP, B.A., B.Sc.

A method is described which enables the effect on the thermal conductivity of a wire of twisting the wire to be measured. In each of the steel, aluminium, copper and lead wires tested the twist decreases the conductivity along the wire by a small amount which is approximately proportional to the square of the twist per unit length.

The change of electrical conductivity is found to be in general less than the change of thermal conductivity, but is also approximately proportional to the square of the twist per unit length.

In the discussion, Mr. C. R. Darling said that the method described seemed an admirable one, but wished to know whether the wires were annealed before the experiment? The initial condition of the specimens would doubtless affect the results obtained, and might account for the discre-



pancies between the conclusions arrived at by different observers.

Mr. Rollo Appleyard also referred to the effect of annealing the wire under test, and added that the effect of stretching on resistance is at least as important as that of twisting. In stranding copper wires for a cable the outer wires are stretched as well as twisted, and any permanent increase of resistance due to such causes is of some consequence in practice. It would be interesting if the experiments could be carried out on a large scale, instead of on a laboratory scale.

Prof. A. O. Rankine inquired whether the effect differs according as the direction of twist is clockwise or counter-clockwise as viewed in the direction of flow of the heat or electric current.

Mr. F. E. Smith suggested that the experiments might be simplified by means of an arrangement for producing a potential difference between the two clamps *C*, shown in the paper, at the ends of the wire. The necessary heating would be effected by the current thereby set up along the wire, which would have a maximum temperature at its middle point owing to the cooling effect of the masses of metal at its ends. The required thermal and electrical measurements could be made by means of wires twisted on to the principal wire as described in the paper.

Dr. Alexander Russell expressed his admiration for the methods of measurement devised by the authors. He pointed out that the twisting of the strands in a stranded cable produces a somewhat similar effect.

Prof. Lees, in reply, said that the wires were soft and not annealed. The object of the experiments was to test the electron theory of conduction, and it was sufficient for this purpose that the state of the wire should merely be the same for the electrical as for the thermal measurements. The large scale tests which had been suggested presented attractions for the engineer, but any accuracy lost by performing the experiments on a small scale was fully compensated by the more precise methods available in a laboratory, while the relatively small cost of the latter methods is a serious consideration to the physicist. The effect of stretching has been investigated by Johnstone, and a reference to his work is given in the paper. The thermal conductivity is increased by stretching while the

electrical conductivity is diminished—another instance of failure in the relation predicted by the electron theory. Prof. Rankine's suggestion was an interesting one. It had been considered, but rejected as improbable; it might, however, be worth investigation. The method suggested by Mr. Smith was somewhat similar to that of Jäger and Diesselhorst, but the latter requires the thermal flow to pass through joints, and inaccuracies arise from this circumstance. As regards stranded cables, the effects of twisting and stretching are in opposite directions for thermal conductivity, but aid one another in the case of electrical conductivity, so that the matter would probably repay investigation.

*The Use of the Wien Bridge for the Measurement of the Losses in Dielectrics at High Voltages, with Special Reference to Electric Cables*, by A. ROSEN, B.Sc., A.M.I.E.E.

In the preliminary section, the loss angle of an imperfect condenser is defined, the equations for the Wien bridge are derived, and the effects of variations of frequency and voltage on the balance are discussed.

One of the difficulties in the application of large potential differences to a bridge is the effect on the arm which has to withstand the high voltage. In the arrangements due to Monach and Schering, this arm is the known condenser; in the bridge as used by the author, the voltage is applied to the ratio coils. The errors introduced by earth impedance are eliminated by using the Wagner auxiliary bridge.

The applications to measurements on cables are considered, and the use of the double bridge in determining the "wire-to-wire" and "wire-to-sheath" losses in a multi-core cable is described.

*An Experiment on the Production of an Intermittent Pressure by Boiling Water*, by CHAS. R. DARLING, F.INST.P., F.I.C.

If a glass tube, open at both ends, and of about 5 mm. bore, be placed in a beaker of briskly boiling water so as to rest on the bottom of the beaker, steam bubbles will be observed to form at the point of contact, causing the water to rise to a definite height in the tube. The column of water thus raised sinks after a time, and then rises again, the rising and falling occurring at irregular intervals. If, however, the tube be narrowed to a bore of about 1 mm.

near the top of the water, and widened out considerably just above the water surface, it will then be seen that the phenomenon becomes regular in action. After rising to the height of about 3 cm. in the widened part, the water discharges back again into the beaker, and after a short interval again rises and is discharged, the cycle being repeated indefinitely.

The explanation appears to be that the water is superheated at the points of contact of the tube and beaker, so that the steam produced can sustain a higher pressure of water. When the water reaches the widened part, however, it is cooled and increases in density until the extra steam pressure at the bottom of the tube is overcome, when it discharges completely. The capillary bore slows down the rate of flow in both directions, and so causes the movements to be steady. A separating funnel with open tap and short stem is well suited to the experiment.

It will be observed that the arrangement constitutes a simple heat engine, with source and sink, automatically passing through a regular cycle of operations, and forms a useful lecture demonstration of the conversion of heat into work.

A Demonstration of *A Novel Instrument for Recording Wireless Signals* was given by N. W. McLACHLAN, D.Sc., M.I.E.E.

The device consists essentially of a drum of Swedish iron with an annular recess, in which are situated coils of fine wire, the ends of the coils being connected to corresponding slip rings. The periphery of the drum is faced with cast iron rings which are machined to run true to 0.0001 in. A small steel shoe rides on the rings, and side play is prevented by a brass guide-piece with a projection which fits into the annular recess. At each end of the guide-piece a hook is formed, and one of the hooks is connected by a light rod to a duralumin lever pivoted to turn in a horizontal plane. A silver syphon passes through the lever from an ink well overhead, and rests lightly on a moving paper tape. To the other side of the lever is attached a strong spring whose tension can be varied, while the remaining hook is attached to a light spring which prevents the shoe from rocking on the drum.

The drum is revolved by a small electric motor, and when a current flows in one of the coils the shoe is attracted to the drum

and a large pull is required to prevent relative motion of the two. This pull is used to actuate the syphon lever mechanism so that the transverse movement over the paper tape inscribes the incoming message as a series of rectangles, the tops of which represent the dots and dashes of the Morse code.

The tangential pull on the shoe is many times that calculated from the formula  $\mu B^2 A / 8\pi$ , where  $\mu$  = coefficient of friction,  $B$  = flux density at shoe contact, and  $A$  = area of contact. The ratio of the actual to the calculated pull depends on the flux density, and has a maximum value of about 80 for steel or cast iron.

Owing to this phenomenon, which gives amplification, and to the fact that there is no air-gap in the magnetic circuit through the shoe, the instrument is extremely sensitive, and will work at a speed of 150 words a minute with a current of 25 microamperes. It will work in a thermionic valve circuit, and for wireless it is fitted with relay contacts so that incoming messages in Morse may be relayed to a printing or other machine direct.

A meeting of the Society was held on Friday, June 8, when PROF. JAMES G. GRAY, D.Sc., F.R.S.E., Cargill Professor of Applied Physics in the University of Glasgow, delivered a lecture entitled, *A General Solution of the Problem of Finding the True Vertical for All Types of Marine and Aerial Craft*. The lecture was accompanied by demonstrations with gyroscopes, and discussion followed.

#### THE CHEMICAL SOCIETY OF JAPAN.

Papers communicated to the Society:—

*On the Beckmann Transformation of Nitrosoketones*, by SHINTARO KODAMA.

*On the Alleged Phenylglyoxal*, by SHINTARO KODAMA.

*On the Proteins in Fagopyrum esculentum, and their Nutritive Values*, by YOSHIHIKO MATSUYAMA.

*On the Quantities of Tryptophan in Various Proteins*, by YOSHIHIKO MATSUYAMA and TAKAJIRO MORI.

*On the Condensation of Nitriles with Thiamides. Part II. Acetonitrile with Thio-benzamide; and Benzotrile with Thioacetamide, by SEIICHI ISHIKAWA.*

*On the Destructive Action of Nitric Acid upon Phenols, by MOTOE IWATA.*

*On the Ternary System: Ethyl Alcohol—Ethyl Ether—Water, by MASUTARO KONO.*

#### THE INSTITUTE OF PHYSICS.

At the last meeting of the Board, the following Corporate Members were elected:—  
 Fellows: J. H. G. Mönypenny, J. H. T. Roberts, R. C. Richards, G. C. Simpson.  
 Associates: A. Adderley, W. T. Astbury, F. G. C. Bratt, P. A. Curry, G. A. R. Foster, A. E. Owen, and J. H. Smith.

#### “THE JOURNAL OF SCIENTIFIC INSTRUMENTS.”

The preliminary arrangements in connection with the regular publication of *The Journal of Scientific Instruments* have now been made by the Institute of Physics in co-operation with the National Physical Laboratory. The special attention of those workers who have new designs for instruments is called to the fact that the Journal is to serve as a medium of publication of detailed descriptions and critical surveys of the behaviour of such instruments. Original papers or laboratory and workshop notes dealing with the practical or theoretical aspects of scientific instruments should be sent to the Editor, Dr. John S. Anderson, The National Physical Laboratory, Teddington, Middlesex.

#### GENERAL NOTES.

In the House of Commons recently, Mr. Herbert Spencer asked the President of the Board of Trade whether he was aware that on the 8th of March, 1923, an application was made to import one ton each of rosazene B extra and rhodanine B extra; whether permission was refused and the dye user referred to British dyemakers; whether the British price quoted was £1,736 more for the two tons of dyeware; and whether, in view of the large amount of unemploy-

ment caused in the dyeing trade by dear dyewares, he would state what steps he proposed to take to remedy this evil?

Sir Philip Lloyd-Greame replied: The applications to which the hon. member refers were, I understand, made by the British Cotton and Wool Dyers' Association. They were refused by the Dyestuffs Advisory Licensing Committee after full consideration of all the circumstances relating to the particular consignments in question, and I do not propose to take any action in the matter. I am unable to assent to the proposition that the establishment of a dye-making industry in this country is injurious to employment in the dyeing industry. The former is, on the contrary, essential to the security of the latter.

Sir Wilfrid Sugden and other Members asked the President of the Board of Trade whether his attention had been drawn to the description in the press of a method of treating gas by a Mr. Tully, whereby, so it was alleged, the percentage of carbon monoxide was very greatly reduced; and whether he had any information as to the practicability of producing such a gas upon a commercial scale?

Sir Philip Lloyd-Greame said: The latest analysis which I have seen of gas produced by Tully plant at present in industrial use, which was published on the 16th May in the *Gas Journal*, gives the carbon monoxide content as 37 per cent., but I observe that in a prospectus just issued, it is stated that by means of a new converter the carbon monoxide content can be reduced to a negligible quantity. I am not in a position to express an authoritative opinion as to the practicability of producing town gas on a commercial scale by the new process. The matter is, however, being carefully watched by the Government Departments concerned.

Mr. Darbishire asked the President of the Board of Trade if he was aware that it was not with the approval of the Colour Users' Association that the distribution of reparation dyestuffs was transferred from the Central Importing Agency to the British Dyestuffs Corporation, and that on many occasions the prices of reparations dyes was more than the prices at which they could be obtained from Germany under licence; and if he would consider the advisability of removing all restrictions upon the free import of foreign dyestuffs?

Viscount Wolmer, Under-Secretary to the Board of Trade, replied: In answer to the first part of the question, the Chairman

of the Colour Users' Association has publicly expressed (the last occasion being on the 14th April) the Association's appreciation of the manner in which the distribution of reparation dyestuffs has been handled by the British Dyestuffs Corporation. As regards the second part, an advisory committee on prices has been formed, on which two out of the four members are representatives of the Colour Users' Association. The answer to the last part of the question is in the negative.

### NOTES ON THE ESTIMATION OF TUNGSTEN IN ORES.

By J. R. POUND, M.Sc.

The following notes sum up the writer's experience, which extended over a very busy period of some three years, dealing with wolfram ores and concentrates. The three methods for the estimation of tungsten that are discussed below are well known, but these results of their trials and comparison under technical conditions may be interesting.

*Method 1.*—The routine procedure for the assay of rich wolfram ores or concentrates was as follows:—Take 1 gram of finely-ground sample; digest with HCl and HNO<sub>3</sub> for about 2 hours, evaporating down to near dryness. To the remaining 5 cc., say, of liquid, add water, warm or boil for  $\frac{1}{4}$  to  $\frac{1}{2}$  hour, filter through a small filter paper, and wash the beaker and the insoluble matter (WO<sub>3</sub>, SiO<sub>2</sub>, etc.) in the beaker at this stage. Then place a weighed porcelain dish under the filter funnel and wash the beaker and the filter paper with successive small quantities of strong NH<sub>4</sub>OH, finally bringing all the insoluble matter on to the filter paper, and collecting the ammoniacal filtrates in the porcelain dish. Then place the filter paper with the insoluble matter in a porcelain crucible, dry and burn off the paper, cool, and brush the contents of the crucible on to an agate mortar, grind ff to flour, and brush this back to the original beaker without loss. In the absence of draughts this can be done safely. Re-treat this residue with acid and ammonia as above, running the second ammoniacal filtrate into the previous porcelain dish, which in the meantime has been heating on a water-bath. Finally evaporate to dryness on the water-bath the combined ammoniacal filtrate, and then heat

gradually to a red heat over a Bunsen burner, cool, and weigh. Then the contents of the porcelain dish give the WO<sub>3</sub> (tungstic acid) directly.

The final filter paper and insoluble matter may be ignited in a porcelain crucible, thus giving the "insoluble matter." If the ore is only wolfram with insoluble matter, which is often the case, then

$$\left(\text{per cent. WO}_3 \times \frac{4}{3} + \text{per cent. insol.}\right)$$

should reach 100 per cent., and this is sometimes a useful check. Pure wolfram (FeMn) WO<sub>4</sub>, contains about 76 per cent. WO<sub>3</sub>. Some authorities quote a maximum value of 76.6 per cent. WO<sub>3</sub>, but the Tasmanian wolfram best known to the writer contained at the most 75.8 per cent. WO<sub>3</sub>.

*Notes on Method 1.*—(1) The attack of HCl or aqua regia on wolfram produces the insoluble WO<sub>3</sub>, and thus the action is slow, and the last portion of the wolfram is liable to be protected from decomposition. Fine grinding is essential, therefore, and especially for material containing over 58 per cent. of WO<sub>3</sub>—i.e., over 50 per cent. of wolfram. The actual assay sample of such material must be ground to flour in an agate mortar. This is easier said than done. Also, during the acid treatment the sample is liable to "crust up" and thus to protect the lower layers from the action; this crust should be broken up several times during the action. When products containing less than 50 per cent. wolfram are ground, and the wolfram is the softest constituent, then a ground product is easily obtained in which all the wolfram is fine enough to be completely and readily decomposed by acids; and if the other constituents of the ore are insoluble in the acids, their presence keeps the wolfram particles separated, and considerably helps the complete decomposition of the wolfram, and in this case the second acid and ammonia treatment is unnecessary. Such common constituents of wolfram ores are silica, silicates, and cassiterite.

(2) The writer could see little if any advantage accruing from prolonged action of HCl alone; therefore, after treatment with HCl for about  $\frac{1}{4}$  hour the HNO<sub>3</sub> was added and the solution slowly evaporated down. The usual amounts of acids were about 40 cc. HCl and 5 cc. HNO<sub>3</sub>, and the time of treatment would vary from 1 to 3 hours. It is doubtful if prolonged action of acid is worth the time—i.e., probably the bulk of the wolfram is decomposed within an hour.

The second acid treatment, necessitated by the imperfect grinding or the incomplete decomposition in the first case, is completed in a short time—say,  $\frac{1}{2}$  hour. Evaporation of the acid right to dryness is liable to render the  $WO_3$  difficultly soluble in ammonia.

(3) It is necessary to wash the  $WO_3$  on the filter paper with strong ammonia, otherwise colloidal silica will run through and ultimately be weighed as  $WO_3$ . It is not necessary to add ammonium chloride to the ammonia wash liquor, and the presence of excessive ammonium chloride with the ammonium tungstate in the porcelain dish causes the contents to flake and jump off the dish during the ignition, thus producing mechanical loss of  $WO_3$ . The ammonia washing of the  $WO_3$  sometimes becomes slow; possibly the silica (or silicic acid) clogs the pores of the filter paper. It is thus best to bring the bulk of the insoluble matter on to the filter paper only with the last ammonia washes. The ammonia filtrate should fit comfortably in an 80-cc. porcelain dish.

(4) The use of a water bath is recommended, as the ammoniacal liquor then evaporates to dryness quietly and safely, and needs no watching.

(5) In this method there is a tendency for colloidal silica to run through with the ammonia liquor, but this may be kept at a minimum by the conditions described under note (3). If the ammoniacal filtrates are collected in a platinum dish the  $SiO_2$  may be removed by the usual  $H_2SO_4$  and HF treatment, and this treatment might be necessary for low-grade material containing easily decomposable silicates; it was not adopted in the work covered by these notes.

The filtrate after the first acid treatment can be tested, after dilution, with  $H_2S$ , and thus  $CuS$ ,  $Bi_2S_3$ , etc., can be precipitated and qualitatively and quantitatively estimated, and afterwards, of course, other constituents of the ore—*e.g.*, the calcium from scheelite,  $CaWO_4$ —can be detected and estimated in the usual way.

The final insoluble matter may be inspected for silica or rock minerals (white), titaniferous iron ore (black), and especially for cassiterite (after the acid treatment,

brownish). Such an inspection, after a little experience, will enable the tin content of the wolfram concentrates to be estimated to the nearest per cent., especially when the amount is small—say less than 5 per cent. Sn. In any case the tin content of the sample may be obtained with accuracy by Pearce's method applied to this insoluble matter—*i.e.*, by fusing it with  $Na_2O_2$ , dissolving the melt in HCl, reducing the strongly-acid hot solution with nickel, cooling in  $CO_2$ , and diluting and titrating the  $SnCl_2$  solution with an iodine solution which has been standardised similarly against pure metallic tin. The writer found this to be the most satisfactory method of estimating the tin in all cassiterite-wolfram concentrates.

When dealing with or purchasing various and unfamiliar wolfram concentrates, the above acid method thus enables the other constituents to be detected and estimated, if necessary, with the minimum of trouble, and this is an important feature. Nevertheless, as will be seen later, with concentrates rich in wolfram care is necessary to avoid low results for the tungstic acid content, and in general the higher of two duplicates will give the more correct per cent.  $WO_3$ . The common tendency is for some of the wolfram to remain unattacked or for some of the  $WO_3$  to remain occluded as ammonium tungstate in the filter paper. In the latter case the yellow  $WO_3$  will be seen in the final ignited insoluble matter. By this method duplicate results should agree to within 1 per cent. of the wolfram content of the sample.

*Method 2.*—A modification of the above method, which obviates the last-mentioned source of error, is to grind *perfectly* at the start so as to ensure complete decomposition of the ore in one acid treatment, and, after washing the  $WO_3$  free from acid, to place it, filter paper and all, in AmOH solution in a graduated flask or beaker (the original beaker may serve), and after its dissolution as ammonium tungstate to make up to the definite volume, and then to take of the clear supernatant liquid a definite aliquot part, which, on evaporation to dryness and ignition, gives the  $WO_3$ , and hence the per cent.  $WO_3$  of the sample is calculated. This method does not necessarily demand complete disintegration of the ore in one acid treatment, but such would be advisable. Excepting that the remaining insoluble matter is not directly

collected, this modified acid method is perhaps better than the previous one—*i.e.*, it is inclined to give higher results for the per cent.  $\text{WO}_3$ .

*Method 3.*—The writer also used the well-known mercurous nitrate method of estimating tungsten, and by this means correct results may be obtained. This method was carried out as follows:—Take  $\frac{1}{2}$  gram of wolfram concentrates and fuse with  $\text{NaOH}$  in a nickel dish for 15 minutes; then dissolve the melt in hot water, a little  $\text{Na}_2\text{O}_2$  being added, and then filter hot from the insoluble  $\text{Fe}$  and  $\text{Mn}$  oxides, unattacked  $\text{SnO}_2$ , etc., and wash well with hot water. Then slightly acidify the filtrate with  $\text{HNO}_3$ , heat till the  $\text{CO}_2$  escapes and the separated silicic acid (and stannic acid) is coagulated, and then make alkaline with ammonia, heat and filter, and wash. Again slightly acidify the filtrate with  $\text{HNO}_3$  and precipitate the tungsten as mercurous tungstate,  $\text{Hg}_2\text{WO}_4$ , a pale yellow coagulable precipitate, by the addition of  $\text{Hg}_2(\text{NO}_3)_2$  solution. This last step demands a nearly neutral solution, but as the  $\text{Hg}_2(\text{NO}_3)_2$  solution can only be made with excess  $\text{HNO}_3$ , the assay solution becomes more acid during the precipitation; small excess of  $\text{Hg}_2(\text{NO}_3)_2$  is added and then dilute  $\text{AmOH}$  drop by drop till the liquor is neutral or slightly acid, when all the tungsten is precipitated as  $\text{Hg}_2\text{WO}_4$ , along with more or less black  $\text{Hg}$  and mercury amino-compounds. As  $\text{Hg}_2\text{WO}_4$  is soluble (with decomposition) in excess of  $\text{AmOH}$  or of  $\text{HNO}_3$ , the conditions of precipitation must be carefully observed, otherwise it is possible to leave tungsten in the solution. The tungsten bearing precipitate is well washed with hot water containing a little  $\text{Hg}_2(\text{NO}_3)_2$ , the precipitate is dried, placed in a porcelain crucible, and ignited, and the resulting  $\text{WO}_3$  is weighed.

This is probably, when combined with suitable modifications (*vide note "5"* above), the most accurate method of separation of the tungsten from all other constituents of most wolfram ores, *e.g.*— $\text{SiO}_2$ ,  $\text{SnO}_2$ ,  $\text{Nb}$ , and  $\text{Ta}$ ; but it is not suitable for scheelite or for ores containing  $\text{Ca}$  and similar metals, appreciable metallic sulphides, especially arsenical pyrites, or phosphates, in which cases the acid method is preferable. In the  $\text{Hg}_2(\text{NO}_3)_2$  method the "fiddling about" necessary to ensure

the complete precipitation of the wolfram takes time, and also the other constituents of the original ore are not separated in a form in which they can be readily detected or estimated, and finally this method is rather expensive. These facts, and the almost general adoption of the acid method by others (buyers or sellers), led to the restricted use of the  $\text{Hg}_2(\text{NO}_3)_2$  method.

The following table will indicate some results on wolfram ores or concentrates obtained by means of these three methods. The figures quoted are in all cases the means of duplicates. The results by methods (1) and (3) were obtained by the writer on the same bulk assay sample; the results by method (2) were obtained by an independent assayer on his own sample, and thus between (1) or (3) and (2) there is a possible divergence due to the two samplings, but as these were carried out on approximately 5-ton parcels of the fine material (minus 6 mesh), shipped in bags of 1 cwt. capacity, the possible errors of sampling should be very small.

Percentage weight of tungstic acid ( $\text{WO}_3$ ) in wolfram ores as determined by—

	(1) The stock acid method.	(2) The modified acid method.	(3) The $\text{Hg}_2(\text{NO}_3)_2$ method.
	p.c. $\text{WO}_3$	p.c. $\text{WO}_3$	p.c. $\text{WO}_3$
(a)	71.3	72.4	72.6
(b)	68.8	69.6	69.8
(c)	67.3	67.1	67.4
(d)	68.2	—	68.1
(e)	59.2	—	59.5
(f)	71.3	—	72.4
(g)	—	71.5	72.4
(h)	64.6	65.3	—

It will be seen that method (1) tends to give the lowest results, which occasionally are below those of methods (2) and (3) by more than desirable limits, which may be placed at 0.6 per cent.  $\text{WO}_3$  on this class of material, *e.g.*—(a), (b), and (f). Method (2) agrees well with method (3), but the latter method inclines to give the higher results. It need only be stated, in conclusion, that the above results represent average results obtained in the writer's practice.

(From the Proceedings of the Australasian Institute of Mining and Metallurgy, Sept., 1922, pp. 291-6.)

## NOTICES OF BOOKS.

*Theoretical Chemistry*, by PROF. W. NERNST, PH.D. Revised in accordance with the eighth-tenth German edition by L. W. CODD, M.A. Pp. XX. + 992. London: Macmillan & Co., Ltd., St. Martin's Street, W.C. 1923. Price 28s. net.

The English translation of Prof. Nernst's well-known volume on Theoretical Physical Chemistry has now reached its fifth edition.

The important advances in physics and chemistry made since the appearance of the previous edition, some seven years ago, have necessitated additions and alterations in some chapters. That on *Radioactivity* has been re-written, and recent work on the *Atom* and in X-ray Spectroscopy has been incorporated.

One or two minor but obvious slips have been noted. These do not detract from the great value of this important work.

*The Examination of Hydrocarbon Oils, and of Saponifiable Fats and Waxes*, by PROF. DR. D. HOLDE. Authorised translation from the fifth German edition by EDWARD MUELLER, PH.D. Second English edition. Pp. XIX. + 572. London: Messrs. Chapman & Hall, 11, Henrietta Street, W.C. 1922. Price 30s. net.

This second English edition, which brings Prof. Holde's valuable technological work up-to-date and available for English readers, has been based upon the fifth German edition, which appeared soon after the conclusion of the war. It therefore contains much new matter. Some of this has been commendably well condensed into tables, where this mode of treatment was possible.

Of the other new matter, English scientists and chemists will be perhaps most interested in the many revelations of the extremities to which German industry was driven towards the close of the war by the lack of fats and oils. Hydrolysis of fats for soap production was forbidden, and oils of any use for food could not be used for varnishes, etc. Every possible source of fat, including such remote material as grape seeds and beech nuts, was exploited.

The general subject, as indicated in the

title, is very fully covered, and there is a mass of information upon those points for which a book of this kind would be consulted. It should prove of great value to technical and analytical chemists.

## BOOKS RECEIVED.

*Experimental Researches and Reports*, by DEPARTMENT OF GLASS TECHNOLOGY. Pp. 138. Vol. V. 1922. Department of Glass Technology, The University, Sheffield.

*Klinische Kolloidchemie*, by DR. ERNST JOEL, MIT EINEM GELEITWORT VON PROF. DR. K. SPIRO. Pp. 124. 1923. Von Theodor Steinkopff, Dresden und Leipzig. 2s. 2d.

## PUBLICATIONS RECEIVED.

The U.S. Department of the Interior have issued the following bulletins:—

Bulletin 686: *Structure and Oil and Gas Resources of the Osage Reservation, Oklahoma, and Structure Maps*, by DAVID WHITE and others. Pp. 427.

Bulletin 736-H.: *Stratigraphy of the El Dorado Oil Field, Arkansas, as determined by Drill Cuttings*, by JAMES GILLULY and K. C. HEALD. Pp. 8 + VI.

Bulletin 480: *Surface Water Supply of the United States, 1918. Part X.—The Great Basin*. Pp. 271.

Bulletin 483: *Surface Water Supply of the United States, 1918. Part XII.—North Pacific Drainage Basins. B. Snake River Basin*. Pp. 171.

Bulletin 508: *Surface Water Supply of the United States, 1919-1920. Part VIII.—Western Gulf of Mexico Basins*, by NATHAN C. GROVER and C. E. ELLSWORTH. Pp. 186.

*Gold, Silver, Copper, Lead and Zinc in Nevada in 1921. Mines Report*, by C. C. HEIKES.

*Gold, Silver, Copper, Lead and Zinc in Idaho and Washington in 1921. Mines Report*, by C. N. GERRY.

*Mineral Waters in 1921*, by W. D. COLLINS.

*Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1921. Mines Report*, by CHARLES W. HENDERSON. Pp. 467-477.

*Gold, Silver, Copper, Lead and Zinc in Colorado in 1921. Mines Report*, by CHARLES W. HENDERSON. Pp. 479-511.

*Economic Geology of the Summerfield and Woodsfield Quadrangles, Ohio, with descriptions of Coal and other Mineral Resources except Oil and Gas*, by D. DALE CONDIT. Pp. 156.

*Manganese Deposits of East Tennessee*, by G. W. STOSE and F. C. SCHRADER. Pp. X., 154.

*Metal-Mine Fires*, by DANIEL HARRINGTON, BYRON O. PICKARD, and H. M. WOLF-LIN.

*Quarry Accidents in the United States during the Calendar Year 1921*, by WILLIAM W. ADAMS.

*Talc and Soapstone—Their Mining, Milling, Products and Uses*, by RAYMOND B. LIADOO.



THIS list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancey Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### *Latest Patent Applications.*

- 12999—Compagnie de Bethune.—Manufacture of sulphovinic acid from ethylene. May 15.
- 13364—Goldschmidt Akt-Ges., T.—Production of silicon-containing aluminium alloys. May 18.
- 12969—Indurit Products Co., Ltd.—Production of articles of the phenol formaldehyde condensation product type. May 15.

13246—Soc. of Chemical Industry in Basle.—Manufacture of intermediate products for azo dyestuffs. May 17.

#### *Specifications Published this Week.*

- 171684—Simonson, W. H., & Mantius, O.—Process for reclaiming sludge acid in petroleum refining.
- 196993—Atack, F. W.—Process for sulphurising organic compounds.
- 186572—Lefranc et Cie.—Process for the manufacture of butyric acid and other fatty acids with recovery of the gases of fermentation.
- 197061—Wolvekamp, M. E.—Colloidal compounds of antimony sulphide.
- 197060—Wolvekamp, M. E.—Soluble preparations of colloidal sulpharsenites.
- 197223—Baumgartner, E.—Manufacture of chromate of soda.
- 189432—Farbwerke Vorm. Meister Lucius & Bruning.—Manufacture of formaldehyde.

#### *Abstract Published this Week.*

195444—Process for reduction of grain.—Chemical Eng. Co. (Manchester), Ltd., & Spensley, J. W., 49, Deansgate, Manchester.

Grain is reduced by treatment in a combination of break rolls, or other ordinary milling appliances, with high-speed centrifugal pin-disc mills. The grain may be subjected to lighter treatment in the earlier break rolls and the final tailings, consisting mainly of bran, are then treated in a pin-disc mill to obtain a further yield of flour. Or fewer sets of break rolls may be employed. The earlier break rolls, except the first, may be replaced by pin-disc mills which are run at a lower speed. The air blast produced by the disc mills may be utilised to perform a preliminary separation of the product.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

195295—Alumina.—Pedemonte, A. L., 2, Rue Emile-Zola, Toulon, France.

*Alumina; aluminium chloride and sulphide.*—Pure alumina is obtained from ferruginous bauxite by heating in a reducing atmosphere to render the iron and titanium magnetic, separating these impurities by magnetic action, dissolving the purified bauxite in hydrochloric or sulphuric acid, digesting to render silica and any remaining titanium insoluble, filtering, and evaporating the filtrate to dryness and calcining the aluminium salt to obtain alumina and recover the acid.



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3297.

## A NOTE ON THE ATOMIC WEIGHT OF TITANIUM.

By F. H. LORING.

In the *Journal of the American Chemical Society* for May 1923, p. 1228, G. P. Baxter and G. J. Fertig announce in a preliminary paper a new determination of the atomic weight of titanium by the analysis of titanium tetrachloride. The value obtained from an average of four fairly concordant analyses is 47.88, which may be rounded off to 47.9. The present but older value obtained by Thorpe is 48.1. The mean of the values = 47.99.

In this *Journal* (1920, CXXI., 105), the present writer developed a scheme for evaluating certain atomic weights based upon the existence of certain isotopes, but the calculated atomic weight of titanium was incident upon hypothetical isotopes 48 and 50. They may be 48 and 46, as the following calculation will show.

If the starting values in the scheme are  $11 \times 4 + 4 = 48$  and  $11 \times 4 + 2 = 46$ , then the calculation becomes:  $(4^3 \times 48 + 2^1 \times 46) / (4^3 + 2^1)$ , and the value, which is a mean one, comes out 47.94. The *a, b, c, d*, values, 1, 2, 3, 4, respectively, have either to be raised to the *third or first* powers. In this case  $4^3 = 64$  and  $2^1 = 2$ , obviously, as previously indicated in principle, with satisfactory results in some instances; e.g., nickel, which involved  $2^3$  and  $4^1$ .

## THE ELECTROMETRIC TITRATION OF MOLYBDENUM WITH A TITANOUS SALT.

By H. H. WILLARD AND FLORENCE FENWICK.  
[Contribution from the Chemical Laboratory of the University of Michigan.]

### INTRODUCTION.

The reduction of molybdic acid to a salt of pentavalent molybdenum by means of trivalent titanium was observed by Knecht and Hibbert.<sup>1</sup> They failed in the attempt

<sup>1</sup> Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co., 1918, p. 99.

to base a volumetric method for the determination of molybdenum upon this fact because of the lack of a suitable indicator for the end-point. An investigation of the applicability of the electrometric titration showed that the reaction is sufficiently rapid for this to be used. The character of the end-point with the polarised bimetallic electrode system with platinum electrodes is essentially as has been described for other titrations.<sup>2</sup> After enough of the titrating solution has been added for equilibrium to be established, there is practically no further change until within about 0.5 cc. of the end-point. The potential difference increases slightly, decreasing again on the addition of excess titanium. Normally the maximum is perfectly definite when the titration is carried out slowly as the end is approached so that equilibrium may be maintained. Otherwise a transient and irregular decrease in e.m.f. may occur before the reaction is quite complete. It is safest to add several drops more of the titanous solution after the supposed end-point has been reached to insure that the potential decrease is permanent and increasing. The reduction is not ideally fast. For this reason it is probable that a better end-point would be obtained with the usual monometallic electrode system. This point was not investigated.

The acid concentration of the molybdenum solution is an important factor; 5-10 per cent. by volume of conc. hydrochloric acid is the most desirable; too high a concentration weakens the reducing power of trivalent titanium appreciably. Sulphuric acid is unsatisfactory. Heat increases the velocity of the reaction but is unnecessary except in special cases.

### TITRATION OF SODIUM MOLYBDATE WITH TITANOUS SULPHATE.

An approximately 0.017 M solution of c. p. sodium molybdate was titrated with titanous sulphate<sup>3</sup> standardised by the method of Thornton and Chapman<sup>4</sup> against ferric sulphate prepared from electrolytic iron of known purity.

<sup>2</sup> Willard and Fenwick, *Jour. Amer. Chem. Soc.*, 1922, XLIV., 2516.

<sup>3</sup> Prepared by the electrolytic reduction of titanous sulphate and stored in an atmosphere of hydrogen.

<sup>4</sup> Thornton and Chapman, *Jour. Amer. Chem. Soc.*, 1921, XLIII., 91.

Table I.

TITRATION OF PURE SODIUM MOLYBDATE  
WITH TITANOUS SULPHATE.

The solutions contained about 8 per cent. by volume of conc. HCl and were heated to about 80°. 0.05 N Ti factor against Fe, 1.4002.

0.017 M Na <sub>2</sub> MoO <sub>4</sub> taken	0.05 N Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> req.
5.00	2.17
10.00	3.92
15.00	5.61
20.00	7.42

A finite excess of the titanous solution is required over that theoretically necessary for a reduction to the pentavalent state. This excess must be independent of the total amount of molybdenum present, and may be determined by titrating solutions of varying molybdenum content and solving the equation,  $n(a-x) = (b-x)$ , where  $a$  and  $b$  are the number of cubic centimetres of the titrating solution required for 2 solutions of known molybdenum content,  $x$  is the required excess, and  $n$  the ratio of the weight of molybdenum in Solution  $b$  to that in Solution  $a$ .

Using the given formula, the excess of titanous solution required to give the end-point was determined from the data in Table I. By combining Expt. 1 with Expts 2, 3, 4,  $x$  was found to be 0.42, 0.45, 0.42 cc., respectively; by combining Expt. 3 with Expt. 4, 0.18 cc. was obtained. The value of  $x$  is to some extent a function of the electrode system used and the magnitude of the polarising voltage. For the most accurate results the titanium solution

should be standardised against a molybdenum solution of known strength, using a volume of the titrating solution as nearly as possible equal to that required for the unknown. It was concluded from the results of a considerable number of titrations that an accuracy greater than 0.1 cc. of 0.05 N solution, which is the equivalent of 0.48 mg. of molybdenum, cannot be claimed for the method.

TITRATION OF MOLYBDENUM IN AMMONIUM  
PHOSPHOMOLYBDATE.

The titration of the molybdenum in a precipitate of ammonium phosphomolybdate is an excellent method of determining the phosphorus content of steels. No special refinements are necessary in standardising the titanous solution for this purpose, since 37.11 mg. of molybdenum corresponds to 1 mg. of phosphorus, and the effect of any slight error in the titration falls far below the limit of accuracy of the precipitation.

After precipitation of the phosphorus in the usual way<sup>5</sup> the ammonium phosphomolybdate is dissolved in ammonia, filtered to remove any iron, and the acidified solution titrated with titanous sulphate. If the precipitate is very large it tends to reprecipitate upon the addition of acid. This may be prevented by the addition of a few drops of phosphoric acid to the ammoniacal solution, but the character of the end-point is thereby altered. In the cold there is no voltage drop with excess of the titrating solution. Just preceding the end-point the normal rise begins, ceases, then continues with increased velocity just as the equivalent point is passed. If the solution

<sup>5</sup> Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, 3rd Edition, 1922, p. 365.

Table II.

## DETERMINATION OF PHOSPHORUS IN STEEL.

	Sample	H <sub>3</sub> PO <sub>4</sub> Sp. gr.	1.7Ti+++ req.	% P from Mo factor	% P from Fe factor	% P Cer- tificate value
Steel	G.	Cc.	Cc.			
0.4 C .....	2.000	1	9.37	0.1016	0.1027	0.102
Bessemer .....	2.001	0	9.57	0.1016	0.1028	...
0.1 C .....	5.003	1	7.20	0.0312	0.0316	...
B. O. H. ....	5.002	0	7.22	0.0313	0.0316	0.031
	5.004	0	7.30	0.0316	0.0320	...
0.1 C .....	2.003	0.5	10.31	0.1116	...	0.112
Bessemer .....	2.001	0.5	10.29	0.1100	...	...

is titrated hot, however, the end-point is perfectly normal and as distinct as in the absence of the phosphoric acid. The separation of titanous phosphate sometimes occurs but has no effect upon the sharpness of the end-point.

Three Bureau of Standards steels were analysed by this method; the results are shown in Table II. The 0.05 *N* factor of the titanium solution against molybdenum was 1.6765; against iron, 1.6956.

The colour of the reduced solution is an extremely intense bluish purple, and forms an excellent qualitative test for molybdenum, even in amounts less than 1 mg. in the absence of tungsten and vanadium.

#### EFFECT OF TUNGSTEN.

One of the most interesting points in connection with the molybdenum titration is the non-interference of tungsten even when present in large amounts. If anything, the end-point is rendered more distinct. Certainly, results seem to be more uniform. There is greater necessity for proceeding slowly near the completion of the titration than when no tungstic acid is present. Very transient decreases in potential occur near the end-point as the titrating solution is added drop by drop, but cease just before the reaction is complete, and the permanent end-point drop is very distinct. The colour is as characteristic as that of the complex phosphate, and is due to an intense blue-black, finely divided precipitate or a solution in case phosphoric acid is also present.

Various amounts of tungsten, in the form of a solution of pure sodium tungstate, were added to 15.00 cc. samples of sodium molybdate, and the molybdenum was titrated. The molybdate was standardised gravimetrically<sup>6</sup>; the 0.05 *N* factor was 1.0005. The titanous solution was standardised against iron; 0.05 *N* factor, 1.2904. All samples contained about 5 per cent. of conc. hydrochloric acid and were titrated cold.

Table III.

EFFECT OF TUNGSTEN.	
0.05 <i>M</i> Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O added	0.05 <i>N</i> Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> req. Cc.
0	15.38
1	15.10
2	15.07
5	15.02
15	15.06
75	15.06

<sup>6</sup> Weiser, *J. Phys. Chem.*, 1916, XX., 657.

If the calculated excess of titanous solution, 0.40 cc. (p. 930), is subtracted from 15.38 cc. it leaves 14.98 cc. The results obtained in the presence of tungsten are in very fair agreement with this theoretical value.

#### SEPARATION OF MOLYBDENUM FROM IRON.

Two methods are in general use for the separation of molybdenum from iron prior to the determination of the former element in steels: (1) precipitation of molybdenum as sulphide from slightly acid solution<sup>7</sup> and (2) precipitation of iron as ferric hydroxide by pouring the acid solution into hot sodium hydroxide solution.<sup>8</sup> An attempt was made to use another method based upon the insolubility of lead molybdate in 2 per cent. perchloric acid. This gives a complete separation from chromium and vanadium. If no other strong acids are present precipitation is complete, but iron is always occluded to some extent and must be removed by treatment with sodium hydroxide, thus detracting from the value of the proposed method.

Synthetic steels were prepared from ferric nitrate and a standard solution of sodium molybdate. The calculated amount of 60 per cent. perchloric acid to form ferric perchlorate and 9 g. in excess was added to each of the samples and the solutions were evaporated until fumes were evolved. A partial dehydration of the molybdic acid occurs, but this presents no difficulties. Chromium, if present, is oxidised and lead chromate, which is much less soluble than the molybdate, will later precipitate. After the evaporated samples were dissolved in water the chromic acid was reduced with a slight excess of ferrous perchlorate. The reduced solutions were heated to boiling and the molybdenum was precipitated by slowly adding to the boiling solution<sup>9</sup> a solution of 10 g. of lead

<sup>7</sup> Johnson, "Chemical Analysis of Special Steels," John Wiley and Sons, 3rd Ed., 1920, p. 156.

<sup>8</sup> Ref. 5, p. 314.

<sup>9</sup> Lead molybdate precipitates immediately and completely in the cold in 5 per cent. perchloric acid in the absence of iron. The latter interferes in the precipitation. With large samples of steel, 2 g. or over, considerable boiling is required for complete precipitation. No precipitation at all occurs in the cold.

perchlorate.<sup>10</sup> The final volume was 300 cc. After the solutions had stood overnight they were filtered through Gooch crucibles, washed with 2 per cent. perchloric acid, then with water, and the precipitates dissolved in sodium hydroxide. The asbestos and ferric hydroxide were filtered off, the filtrates acidified with a 5 per cent. excess of hydrochloric acid, and titrated with titanous sulphate.

Table IV.

DETERMINATION OF MOLYBDENUM IN  
SYNTHETIC STEELS.

In all experiments 1 g. of iron and 0.0720 g. of molybdenum were added. The latter required theoretically 10.00 cc. of titanous solution. This solution was standardised against the standard molybdate solution.  
Cr added V added Ti+++ req Error

Mg.	Mg.	Cc.	Mg. of Mo
0	0	9.95	-0.36
0	0	9.90	-0.72
20	0	10.00	0.0
20	5	9.98	-0.14
20	5	10.00	0.0

SUMMARY.

The reduction of hexavalent molybdenum to the pentavalent state by titanous salts is sufficiently rapid for employment of electrometric titration. This gives a means of determining molybdenum in alkali molybdates accurate to within 0.5 mg. and, indirectly, phosphorus in the precipitate of ammonium phosphomolybdate. Tungstic acid presents no interference, and it also eliminates the necessity of applying a correction for the excess titanous solution required to give the end-point.

Ann Arbor, Michigan.

—(From the *Journal of the American Chemical Society*, 1923, XLV., 928-33.)

<sup>10</sup> Made by dissolving the theoretical quantity of pure litharge in perchloric acid. The oxide was added slowly to the cold, dilute acid, heated to boiling, cooled and filtered.

THE ELECTROMETRIC TITRATION  
OF SELENIUM IN THE PRESENCE OF  
TELLURIUM, IRON AND COPPER.

By H. H. WILLARD AND FLORENCE FENWICK.

[Contribution from the Chemical Laboratory of the University of Michigan.]

INTRODUCTION.

The reduction of selenious acid to metal by titanous chloride was observed by Moser<sup>1</sup> and also by Monnier.<sup>2</sup> Moser attempted to develop a volumetric method for selenium based on this reaction, using methylene blue as indicator, but the results obtained were invariably too high. This was due to the further reduction of the selenium to hydrogen selenide, a compound which had been shown to exist under similar conditions by Pleischl<sup>3</sup> and Trautmann.<sup>4</sup>

Under the condition imposed by Moser, namely, a hot hydrochloric acid solution, the electrometric end-point is either absent or very poor, but in a cold solution containing 25 to 75 per cent. of conc. hydrochloric acid and saturated, or nearly so, with sodium chloride, the end-point with the previously described polarised bimetallic electrode system<sup>5</sup> with platinum electrodes is excellent. The presence of the sodium chloride is important. It insures rapid and uniform coagulation of the selenium hydrosol and increases the sharpness of the change in voltage at the end-point. The use of a cold solution also eliminates the almost inevitable loss of selenium by volatilisation.

The character of the end-point for this titration is somewhat difficult to describe but is readily discovered by experiment. After enough of the titrating solution has been added to give a constant potential, there is little change until within a short distance of the end-point. Slight fluctuations in the e.m.f. may be manifested; the resistance of the solution is so low that the galvanometer is extremely sensitive. The characteristic rise occurs, with the fall im-

<sup>1</sup> Moser, *Z., anal. Chem.*, 1918, LVII., 277.

<sup>2</sup> Monnier, *Ann. chim. anal. appl.*, 1915, XX., 1.

<sup>3</sup> Pleischl, *Kastner Arch.*, XCIII., 430.

<sup>4</sup> Trautmann, *Bull. soc. ind. Mulhouse*, 1891, LXI., 87.

<sup>5</sup> Willard and Fenwick, *Jour. Amer. Chem. Soc.*, 1922, XLIV., 2516.

mediately following. The condition of the solution with respect to acidity and foreign salts determines which of the two predominates. Increasing the polarising e.m.f. from 0.1 to 1.0 volt makes no appreciable difference in the character of the end-point.

As is the case with other titanous titrations, the actual voltage change may not be large, in fact may not amount to more than a few millivolts. The galvanometer should be sufficiently sensitive to give a distinct deflection for a change in potential of 1 mv. between the electrodes.

It is inadvisable to clean the electrodes between titrations more than to wash them with distilled water. The small amount of selenium adhering after the first titration increases the sharpness of the end-point. The coagulation of the colloidal selenium in the near vicinity of the end-point is quite distinct, and affords a fairly close visual check on the titration.

TITRATION OF SELENIOUS ACID WITH TITANOUS SULPHATE.

A pure commercial selenium was dissolved in nitric acid, evaporated to dryness, and the selenium dioxide obtained purified by two sublimations. An approximately 0.05 N aqueous solution of selenious acid was prepared and standardised gravimetrically by reduction with hydrazine sulphate according to the method of Gutbier, Metzner and Lohmann.<sup>6</sup> In four experiments the weights of selenium obtained from 100.00 cc. of the solution were 0.0994, 0.0995, 0.0997, 0.0996 g., or an average of 0.0995 g.

The solution was, therefore, 0.0503 N. The purity of the selenium dioxide was 99.1 per cent., the rest being, doubtless, moisture.

<sup>6</sup> Gutbier, Metzner and Lohmann, *Z. anorg. Chem.*, 1904, XLI., 297.

Table I.

TITRATION OF SELENIOUS ACID WITH TITANOUS SULPHATE.

Total initial volume in all cases, 100 cc.		Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> factor		
SeO <sub>2</sub> taken	Ti <sub>2</sub> (SO <sub>3</sub> ) req.	Av. Ce.	Fe calc. from Ce.	KMnO <sub>4</sub> calc. from Ce.
10.00	6.85			
10.00	6.75	6.80	6.70	6.72
15.00	10.15			
15.00	10.17			
15.00	10.18	10.15	10.05	10.08
15.00	10.10			
20.00	13.52			
20.00	13.52	13.52	13.40	13.44
30.00	20.15			
30.00	20.26			
30.00	20.15	20.19	20.10	20.16
30.00	20.20			
40.00	26.80			
40.00	26.80	26.80	26.80	26.88

Samples of this solution were titrated electrometrically with titanous sulphate<sup>7</sup> in solutions containing 40 per cent. of conc. hydrochloric acid and saturated with sodium chloride. All titrations were conducted in a current of carbon dioxide. The titanium solution was standardised against a solution of ferric sulphate,<sup>8</sup> prepared from electrolytic iron of known purity, and against potassium permanganate.<sup>10</sup> Against

<sup>7</sup> Prepared by the electrolytic reduction of titanous sulphate and stored in an atmosphere of hydrogen. Thornton and Chapman, *Jour. Amer. Chem. Soc.*, 1921, XLIII., 91.

<sup>8</sup> Titrated to the disappearance of the colour of ferric thiocyanate. Thornton and Chapman, *Ref. 7*.

<sup>10</sup> Titrated by adding it to the permanganate in sulphuric acid solution. The permanganate was standardised against sodium oxalate from the Bureau of Standards.

Table II.

EFFECT OF HYDROCHLORIC ACID.

Total initial volume in all cases, 100 cc.

SeO <sub>2</sub> taken	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> required	Vol. of HCl (Sp. gr. 1.18) in 100 cc. of soln.
Cc.	Cc.	Cc.
15.00	11.44	75
15.00	11.40	50
15.00	11.42	35
30.00	22.77	35
15.00	11.43	25
30.00	22.70	25
20.00	15.08	25
10.00	7.53	25
15.00	...	10

Character of end-point.

Very good. Fall at end-point not permanent but definite.  
 Rise and fall extremely sharp.  
 Very good.  
 Very good.  
 Rise more marked than fall.  
 Good.  
 Good.  
 Good.  
 Poor.

the former it was found to be 0.0750 N, against the latter, 0.0748 N.

From a comparison of the volumes of titanous sulphate used in the several determinations it is evident that the excess of the titrating solution required to give the end-point reaction was very close to 0.10 cc. (The titrations with the 40.00 cc. samples were evidently a little low.) When this correction is made, the check with the amount of titanium calculated from the iron factor is usually within 0.02 cc. The titration of the selenious acid proceeds, then, according to the equation:  $\text{SeO}_2 + 4\text{HCl} + 4\text{TiCl}_3 = \text{Se} + 4\text{TiCl}_4 + 2\text{H}_2\text{O}$ . There can be, therefore, no secondary reaction such as found by Moser<sup>1</sup> and no empirical standards are necessary in the determination.

#### EFFECT OF VARYING THE CONCENTRATION OF HYDROCHLORIC ACID.

The effect of varying the hydrochloric acid concentration is shown in Table II.

An acidity of 25 to 75 cc. of conc. hydrochloric acid in 100 cc. of solution is entirely satisfactory.

#### EFFECT OF SULPHURIC ACID.

In the preparation of an actual sample of metallic selenium for analysis it is very desirable to avoid the use of hydrochloric acid for removing the nitric acid in which the material is dissolved. In hydrochloric acid solution selenium chloride is appreciably volatile at the boiling point. For this reason the effect of sulphuric acid upon the titration was studied.

Table III.

#### EFFECT OF SULPHURIC ACID.

15.00 cc. of 0.05 N selenious acid solution was used in each titration. The solutions were saturated with sodium chloride and had an initial volume of 100 cc.

$\text{Ti}_2(\text{SO}_4)_3$	Vol. of conc. acid <sup>a</sup> in 100 cc. of soln.	Character of end-point. (Control titration).
Cc.	Cc.	
11.37	50 HCl	Rise long and marked, fall slow. Titrated to end of rise.
11.40	50 HCl + 5 $\text{H}_2\text{SO}_4$	Not quite as good as the preceding. No permanent fall. Not difficult to determine end-point.
11.40	50 HCl + 10 $\text{H}_2\text{SO}_4$	

<sup>a</sup>Refers to HCl, d. 1.18, or to  $\text{H}_2\text{SO}_4$ , d. 1.84.

The acid may be present in amounts up to 5 or 10 cc. per 100 cc. of solution, but is to be avoided in any considerable quantity.

The non-volatility of selenium in hot sulphuric acid was shown by the evaporation of samples of the selenium solution with 5 cc. of conc. sulphuric acid until dense fumes formed and then titration after the addition of sodium chloride and hydrochloric acid. The maximum variation was 0.06 mg. in a total of 15 mg., or 0.4 per cent. The end-point, however, was not quite as sharp as when the fuming had been omitted.

#### EFFECT OF TELLURIUM.

Of the common associates of selenium, tellurium is probably of the greatest interest in its effect upon the titration of the former element. In a hot hydrochloric

acid solution of moderate concentration tellurium is rapidly reduced by titanous salts, but in the cold the reduction, if any takes place, is very slow.

Metallic tellurium was carefully freed from selenium by Keller's method,<sup>11</sup> reprecipitated as metal, again dissolved in nitric acid, evaporated to fumes of sulphuric acid and dissolved in hydrochloric acid. Various amounts of this solution were added to known amounts of selenious acid solution and determinations made as outlined in Table IV.

<sup>11</sup> Keller, *Jour. Amer. Chem. Soc.*, 1897, XIX., 771. Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, 3rd ed., 1922, p. 423.

Table IV.

## EFFECT OF TELLURIUM.

15.00 cc. of 0.05 N selenious acid was used in each titration. Total initial volume 100 cc.

Ratio, wt. Te:wt. Se	Ti <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> Cc. in 100 cc. of soln.	Vol. of HCl (Sp. gr. 1.18)	Character of end-point.
...	11.34	50	(Control titration)
4:5	11.33	50	Sharp rise, no fall with excess
4:5	11.35	50	Regular fall with excess
8:3	11.35	50	Distinct rise, no fall with excess
4:1	11.35	50	No fall with excess
8:1	11.35	50	No fall
8:1	11.30	25	A fall
8:1	11.35	25	A fall
8:1	11.35	25	No fall. End-point a change in rate of rise

Tellurium even in large amounts does not interfere in the titration of selenium, but it seems to affect the character of the end-point much as does sulphuric acid. The fall in potential as the end-point is passed does not always occur, but the rise is fully as sharp as in the absence of these substances. There is no difficulty in recognising the completion of the reaction.

## EFFECT OF IRON.

One of the most surprising and interesting things in connection with the selenium determination is the fact that the volume of titanium solution used in titrating mixtures of selenium and ferric iron is identical with that for the selenium alone, although ferrous iron is formed during the precipitation. The character of the end-point is much the same as that described later with mixtures of selenium and copper, but no

second end-point is obtainable at the point of complete reduction of both elements.

In Table V. the solutions contained 30.00 cc. of conc. hydrochloric acid in a volume of 100 cc. and were saturated with sodium chloride.

The behaviour of selenium under these conditions seemed at first paradoxical. It was observed, however, that with large amounts of iron the precipitation was apparently incomplete. From two samples, one of which contained twice as much ferric iron as the other, the selenium was filtered at the end of the titration, thiocyanate was added, and more of the titanous solution run in. No sharp colour change occurred. The deep red faded slowly only to reappear in a few seconds. The amount of titanium required for an approximate end-point was twice as much in the solution containing

Table V.

## EFFECT OF IRON.

SeO <sub>2</sub> taken Cc.	0.05 N Fe <sup>+++</sup>		Ti <sup>+++</sup> req. Cc.	Remarks.
	added Cc.			
15.00	...		10.60	
15.00	1		10.58	
15.00	5		10.52	
15.00	10		10.61	
30.00	1		21.25	
30.00	10		21.26	

## Second Series.

15.00	...	10.15	
15.00	25	10.22	Pptn. very incomplete
15.00	35	10.17	Pptn. very incomplete
15.00	50	10.15	Pptn. slight
30.00	50	20.20	Pptn. greater than preceding
10.00	75	6.82	No pptn. End-point a little slow.

double the amount of iron. After much more titanous sulphate had been added there was a further precipitation of selenium. It appeared that ferric iron and selenious acid might form a rather unstable compound in which the selenium is reduced only with difficulty, requiring a large excess of titanium. An amount of ferric iron equivalent to the combined selenium is reduced along with the free selenious acid and the numerical result of the titration, therefore, is unaffected. In the second series the amount of iron was increased until no precipitation occurred, without affecting the results, thus supporting this view. The exact composition of the compound was not investigated.

#### EFFECT OF COPPER.

In hydrochloric acid solution trivalent titanium reduces cupric salts to the cuprous form.<sup>12</sup> When present with selenium,

<sup>12</sup> *Rhead, J. Chem. Soc.*, 1906, LXXXIX., 1491. *Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co.*, 1918. *Moser, Chem.-Ztg.*, 1912, XXXIV., 1126. *Monnier, Ann. chim. anal.*, 1916, XXI., 109. *Mach and Lederle, Landw. Vers. Sta.*, 1917, XC., 191. *Thornton, Jour. Amer. Chem. Soc.*, 1922, XLIV., 998.

however, the latter is reduced first and apparently selectively. The electrometric titration gives two end-points, one when the selenium is entirely precipitated and a second at the completion of the reduction of the copper. Toward the end of the first reaction the voltage starts to rise slightly. There is then a long, distinct, upward swing that marks the end-point, followed usually by continued rise. The copper end-point is a second sharp rise.<sup>13</sup> It is not quite as clear as the first but readily distinguishable after a little experience.

Table VI. records a number of titrations carried out in the presence of copper.

<sup>13</sup> It is obvious that the method may be adapted to the determination of copper alone. A number of very accurate titrations were made in this way, but this application is not stressed because of the rather large amount of other work on this reaction already published.

Table VI.

#### EFFECT OF COPPER.

All solutions titrated had an initial volume of 100 cc., contained 30-40 p.c. of conc. hydrochloric acid and were saturated with sodium chloride.

SeO <sub>2</sub> taken Cc.	0.05 N CuSO <sub>4</sub> added Cc.	Ti+++ req. for Se end-point Cc.	Total Ti+++ used Cc.	Ti+++ req. for Cu Cc.
...	5.00	...	...	3.55
15.00	...	10.50	...	...
15.00	...	10.50	...	...
15.00	5.00	10.53	14.02	3.49
15.00	10.00	10.50	17.60	7.10
15.00	1.00	10.52	...	...
<i>Second Series.</i>				
15.00	...	10.65	...	...
15.00	5.00	10.65	...	...
30.00	5.00	21.24	...	...

#### SUMMARY.

1. The volumetric reduction of selenious acid to selenium by titanous sulphate is rapid and accurate to within 0.1 mg. in cold hydrochloric acid solution saturated with sodium chloride.

2. Under these conditions tellurium is not reduced, and its only effect is to modify the nature of the end-point.

3. Moderate amounts of sulphuric acid have no deleterious effect upon the determination of the end-point and there is no



volatilisation of selenium at the fuming temperature in this acid.

4. The titration of selenium is quantitatively independent of the concentration of iron, although ferrous iron is formed in the reaction.

5. The reducing effect of trivalent titanium upon mixtures containing copper and selenium is selective, the latter being reduced first, and both elements may be determined in a single titration.

. Ann Arbor, Michigan.

—(From the *Journal of the American Chemical Society*, 1923, XLV., 933-9.)

### GENERAL NOTES.

#### NEW COLOUR INDEX.

##### NOTABLE BRITISH ACHIEVEMENT IN DYE TECHNOLOGY.

##### *Dye-Users' Vade Mecum.*

The new "Colour Index," now approaching completion, will add greatly to the prestige of the British dye industry, and at the same time represent one of the most valuable achievements of the Society of Dyers and Colourists. That there should be a thoroughly up-to-date and comprehensive index of dyes is extremely desirable, but up to the present the best available authority has been a German pre-war publication, now inevitably far from complete. Great Britain has the distinction of having produced what has already been accepted by colour manufacturers, dye-users and technological experts throughout the world as a standard work of supreme importance.

##### OLD DYES WITH NEW NAMES.

The stoppage of German supplies of dyes during the war led to the rapid development of existing colour works in other countries and the establishment of important new works. Great strides have thus been made in the production of dyestuffs, and many firms are placing on the market dyes which have new commercial names, but which may not be new in constitution. A number of them are replicas of the German products with which users had become familiar. In the absence of definite knowledge as to their constitution, the dye-user has been at a disadvantage in selecting his dyestuffs, and has been bewildered by the multiplicity of products submitted to him.

From a dye-user's point of view, therefore, it is a matter of great importance to

know all the different commercial names used to denote the particular dye he requires, and the firms who make such products. No such information has been available, for the most comprehensive work of reference on the subject was the *Farbstofftabellen* of Dr. Gustav Schultz, published in 1914, which necessarily lacks information with regard to the great developments which have taken place in this and other countries during the past nine years.

In order to remedy this defect, the Society of Dyers and Colourists, whose headquarters are at Bradford, decided to undertake the work of compiling an up-to-date and comprehensive Colour Index. The arduous work of editorship was placed in the hands of Dr. F. M. Rowe, of the Manchester College of Technology, assisted by Mr. C. Lea, and a Revision Committee was formed under the chairmanship of Mr. Ernest Hickson, of Bradford, on which the leading dyestuff manufacturers and dyestuff users of all classes were represented, as well as the leading professors and experts on the technical side.

##### TO BE FINISHED THIS YEAR.

The Colour Index has been published in monthly parts, the first being issued in September, 1922. In order to ensure the greatest possible accuracy, 150 copies of the proofs of each part are circulated all over the world to colour manufacturers, colour users, and technical experts, and the corrections and suggestions thus embodied have been exceedingly valuable. Fourteen parts are required to complete the Index. The ninth has been issued, and the matter for the remaining parts is now in the hands of the printers. The end of this great undertaking, therefore, is now within sight, and there is no doubt that the remaining five parts will be published before the end of 1923.

##### SCOPE OF THE WORK.

One of the features of the Index, when completed, will be the comprehensive indices which it will contain. These will cover the names of many thousands of commercial dyes, and will also deal with the patent numbers, the intermediate products used, and so on. Some idea of the magnitude of the undertaking may be gained from the fact that the number of distinct synthetic dyes dealt with will exceed 1,320, as against the 1,000 dealt with by Schultz. Most of these dyes have a number of commercial names—many of them thirty or

more—and in all cases these names and the respective makers are given. The products of over a hundred colour-making firms are included, and the matter covers 700 large quarto pages of closely-printed and condensed matter.

A dye user who requires a particular dye can thus find a complete list of the manufacturers who make it, the scientific name of the product, its components and formula, details of its preparation, its discoverer, exhaustive references to the literature on the subject, its properties, uses, and modes of application.

#### MANY INDUSTRIES COVERED.

In addition to the Synthetic dyestuffs, the Colour Index will include the principal colouring matters and the pigments. Dyes are used not only in the great textile industries, but in a large number of other industries, such as the paint and varnish, paper making, soap and oil, in photography, medicine, foodstuffs, and so on. Details are given of dyes specially used in photography, which have not been included in any previous work. There are some particularly valuable references to the suitability of dyes for calico printing, especially with regard to dischargeability.

This great work will supersede all former reference books, and there is no doubt that it will be of great practical as well as scientific utility. It will guide the dye-user safely through the maze of modern dyestuff names, and enable him to make the fullest use of the enormous developments in the dye-making industry in recent years.

#### THE DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH.

The Lord President of the Council has accepted with much regret the resignation of Sir George Beilby, LL.D., F.R.S., after nearly seven years' voluntary service as Director of Fuel Research and Chairman of the Fuel Research Board under the Department of Scientific and Industrial Research. The Board was established in 1917 to investigate the nature, preparation and utilisation of fuel of all kinds.

The Lord President has appointed Mr. C. H. Lander, D.Sc., M.I.Mech.E., A.M.-Inst.C.E., to be Director of Fuel Research, and Sir Richard Threlfall, K.B.E., F.R.S., a present member of the Board, to be Chairman. The Hon. Sir Charles Parsons,

K.C.B., F.R.S., will continue his membership of the Board for a further period. Sir George Beilby retains his membership of the Advisory Council of the Department, and has consented to act as Honorary Adviser to the Board.

The following gentlemen have accepted appointment as additional members of the Board:—

Mr. R. A. Burrows, Sir John Cadman, K.C.M.G., D.Sc., Dr. Charles Carpenter, C.B.E., D.Sc., Mr. Samuel Tagg, Prof. Sir James Walker, D.Sc., LL.D., F.R.S., Prof. R. V. Wheeler, D.Sc.

#### DYESTUFFS (IMPORT REGULATION) ACT.

##### APPLICATIONS FOR LICENCES IN MAY.

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during May, has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee.

The total number of applications received during the month was 497, of which 409 were from merchants and dealers. To these should be added the 17 cases outstanding on May 1, making a total for the month of 514. These were dealt with as follows:—

Granted—304 (of which 293 were dealt with within seven days of receipt).

Referred to British makers of similar products—136 (of which 130 were dealt with within seven days of receipt).

Referred to Reparation Supplies available—53 (all dealt with within two days of receipt).

Outstanding on May 31—21.

Of the total number, 514, of applications received, 458, or 89 per cent., were dealt with within four days of receipt.

*Board of Trade.*

*June 12, 1923.*

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL SOCIETY.

THURSDAY, JUNE 14.

Papers read:—

C. CHREE, F.R.S. *Magnetic Phenomena in the Region of the South Magnetic Pole.* Magnetographs were in simultaneous

operation from April to October, 1912, at the base stations of the British and Australasian Antarctic expeditions. These stations were situated on opposite sides of the south magnetic pole. A comparison is made of the regular diurnal inequalities and the amplitudes of the absolute daily ranges of the magnetic elements at the two stations. The data are employed to illustrate the remarkable sensitiveness of the regular diurnal variations in high latitudes to the presence of magnetic disturbance. The results are also applied to the question of a suitable criterion for the daily activity of magnetic disturbance.

O. R. HOWELL. *The Catalytic Decomposition of Sodium Hypochlorite by Cobalt Peroxide.*

1. The rate of decomposition of sodium hypochlorite solution by cobalt peroxide is directly proportional to the amount of peroxide present.

2. The rate is accelerated by sodium salts and (in the case of sodium chloride) is directly proportional to the square root of the concentration of sodium ions present. This is explained by assuming the mechanism of the reaction to consist in the linkage of hypochlorite ions to the positive oxygen and sodium ions to the negative oxygen of the peroxide, with subsequent immediate decomposition of the quadrivalent oxygen compound. In the presence of a fixed amount of hypochlorite the rate is then proportional to the degree of adsorption of the sodium ions.

3. The rate is retarded by alkali and the retardation is proportional to the adsorption of hydroxyl ions. This is explained by the fact that hydroxyl ions are attracted by the positive oxygen of the peroxide yielding an inactive compound to the exclusion of hypochlorite ions.

4. The rate of the reaction has been measured between 25° and 50°. The average temperature coefficient over this range is 2.37 and the Arrhenius activation coefficient  $E = 16,574$ .

5. The catalyst is not affected by any of the common catalytic poisons.

N. M. HOSALI. *On Seismic Waves in a Visco-Elastic Earth.* Communicated by Prof. L. N. G. Filon, F.R.S.

The effects of viscosity on the propagation of seismic waves are considered, the medium being assumed to obey certain

stress-strain relations given recently by Prof. L. N. G. Filon.

It is found that the waves are subject to damping and dispersion dependent on the period. For each type of wave—dilatational, distortional or surface—there exists a minimum period below which a wave cannot be transmitted, and for any period above the minimum two distinct waves can be propagated, one heavily damped and slow travelling, and one lightly damped and quick travelling.

The observed reduction in the amplitude of oscillations in the main shock, as the epicentral distance increases, indicates that if the material in the outer layers of the earth obeyed the theory here developed, it would have a viscosity of order  $10^8$  or  $10^9$  e.g.s. units. Such a viscosity would have no appreciable effect on the velocity of propagation of earthquake waves.

The vibrations of an incompressible, visco-elastic sphere are briefly discussed, and it is shown that viscosity produces damping and lengthening of period. The oscillatory modes of any species are finite in number and can be divided into two groups, one more heavily damped than the other.

Papers read in title only:—

J. W. LANDON and H. QUINNEY. *Experiments with the Hopkinson Pressure Bar.* Communicated by Sir A. Ewing, F.R.S.

The paper deals with some experiments carried out since the late Prof. Bertram Hopkinson's paper (*Phil. Trans.*, 1914).

It is found that when the firing end of the bar is coned down to a smaller diameter and the time-piece is sufficiently long, the bar itself is left with a negative momentum. A theoretical investigation of the propagation of a pressure wave along a cone of small angle shows that as the wave proceeds along the cone a tail of tensile stress is formed. Experimental results agree fairly closely with theoretical.

The experimental observations show that with a bar of uniform diameter the pressure wave produced by detonation of gun-cotton is considerably distorted as it is propagated, but that the rate of distortion decreases as the wave travels along the bar.

A graph is deduced from experiments showing variation of pressure over cross-section of the bar when a gun-cotton primer is detonated  $\frac{3}{4}$  inch away from the end.

Pressure falls away rapidly as distance from axis of the bar increases.

One of the objects of further experiment was to determine with greater accuracy the maximum pressure produced in the detonation of gun-cotton. It was hoped that the overstrain might be reduced by special heat treatment of the bars, and that the pressure transmitted would be more nearly the true pressure at the firing end. There is no evidence from the experiments that any substantial improvement has been effected by heat treatment except in so far as the life of the bars has been increased.

The highest maximum pressures recorded were 117 tons per square inch for a 1-ounce gun-cotton primer in contact with the end of the bar, and 82 tons per square inch with the primer  $\frac{3}{4}$  inch away from the end. These results were obtained with a short bar of  $\frac{3}{4}$ -inch diameter.

With concrete bars the phenomena exhibited are the same in general as with steel bars, except that the front of the wave appears to be entirely obliterated, and only the part in which pressure is less than the crushing stress of the concrete is propagated along the bar.

S. F. GRACE. *Free Motion of a Sphere in a Rotating Liquid at Right Angles to the Axis of Rotation.* Communicated by G. I. Taylor, F.R.S.

The paper forms a companion to a previous one dealing with the motion of a sphere parallel to the axis of rotation. The density of the sphere is equal to that of the liquid, and the motion a small disturbance from one of uniform rotation like a rigid body; the system is free from bodily forces and initially disturbed by a motion suddenly communicated to the sphere. The subsequent motion of the centre of the sphere is wholly in a plane perpendicular to the axis of rotation (the equatorial plane), and the disturbed motion of the liquid is symmetrical with respect to this plane. The path of the centre of the sphere is a spiral with a definite pole. The sphere winds round the pole in a direction opposite to that of the rotation of the liquid while continually approaching it, the motion being such that the time of a complete turn tends to become constant and equal to one-half the time of a revolution of the undisturbed liquid. The motion of the liquid in the equatorial plane tends rapidly to zero away from the sphere. At points along the prolongation of the polar

axis of the sphere the motion is parallel to the equatorial plane and is a maximum at the sphere. At any point in the sphere the velocity of the liquid relative to the sphere is the component in the tangent plane of a vector of constant magnitude which uniformly describes a right circular cone. Parts of the solution are not applicable for large values of time.

B. F. J. SCHONLAND. *The Passage of Cathode Rays through Matter.* Communicated by Prof. S. Ernest Rutherford, F.R.S.

1. The absorption of cathode rays of velocity  $6.10^9$  to  $1.2.10^{10}$  cms./sec. in various metals has been studied with an arrangement designed to eliminate interference from secondary rays and to measure both the fraction of the beam passed through and that actually absorbed in the foil.

2. The latter fraction varies with thickness and velocity in the same manner for all elements; the nature of the variation of the former depends upon the absorbing material.

3. The conception of a range for these particles is established by two independent methods of measurement.

4. The results are explained by applying the theory of absorption due to Bohr, with which they are in quantitative agreement.

#### THE CHEMICAL SOCIETY.

ORDINARY SCIENTIFIC MEETING, THURSDAY,  
JUNE 21.

The following papers were read:—

*The Constitution of the Higher Oxide of Nickel.* O. R. HOWELL.

*The Relationship of the Tautomeric Hydrogen Theory to the Theory of Induced Alternate Polarities.* F. ALLSOP and J. KENNER.

*Electron Valency Theories and Stereochemistry.* S. SUGDEN.

*The Relative Influences of Water Vapour and Hydrogen upon the Combustion of Carbon Monoxide—Air Mixtures at High Temperatures.* W. A. BONE, D. M. NEWITT, and D. T. A. TOWNEND.

*Metallic Hydroxy-Acid Complexes. Part I.—Cuprilactates.* I. W. WARK.

*Metallic Hydroxy-Acid Complexes. Part II.—Cuprimalates, their Formation, Properties, and Composition.* I. W. WARK.

*Cholesterol and its Role in the Organism.* S. MINOVICI.

THE ROYAL INSTITUTION.  
"ATOMIC PROJECTILES AND THEIR  
PROPERTIES."

On Saturday, June 16, Sir ERNEST RUTHERFORD delivered his postponed lecture on the above subject.

He gave some of the results he and Dr. Chadwick have obtained in the Cavendish Laboratory by utilising  $\alpha$  particles, spontaneously fired from radio-active substances at incredible speeds, in their attempts to disintegrate the atoms of various elements.

Remarkable results have been obtained with certain elements, including boron, nitrogen, sodium, aluminium, fluorine, and phosphorus. Constituents of the atoms of these elements have been expelled by  $\alpha$  particles, and, at least temporarily, something like the transmutation of the elements has been accomplished.

With special apparatus it has been demonstrated that the particles thus expelled are in all cases hydrogen atoms, sometimes in that form and at others in the form of helium nuclei, which consist of four hydrogen nuclei bound together.

It seems almost certain, therefore, that the ultimate "bricks" from which all substance are built up are hydrogen nuclei, the manner in which they are combined in any particular atom determining the nature of the element of which it is a part.

The fact that, when an alpha particle entered the atomic nucleus of substances like aluminium, hydrogen nuclei were frequently projected backwards as well as forwards was a strong corroboration of the theory that the central nucleus of an atom was surrounded by electrons moving rapidly round the nucleus.

The speed and direction of motion of any of these "satellite" electrons, when struck by an intruding  $\alpha$  particle, would depend on its position in its orbit when hit, and Sir Ernest showed by a diagram how, under certain conditions, an electron would be projected in such a way as to sweep close around the nucleus and return on the other side in the same direction as it approached the central region.

Experimental work in this field is very difficult and expensive, but the results are so fundamental in their nature as to promise the solution of many of the problems of physics and chemistry which a few years ago seemed incapable of solution. Among these are the actual transmutation of the elements—and the possibility of harnessing the stupendous energy at present locked up in the complex structure of the atom.

## ROYAL AGRICULTURAL SOCIETY.

PROCEEDINGS AT MONTHLY COUNCIL,  
WEDNESDAY, JUNE 6, LIEUT.-COL. E. W.  
STANYFORTH (PRESIDENT) IN THE CHAIR.  
The Reports of Committees included:—

## CHEMICAL.

Mr. Luddington (Chairman) reported that a list of the samples analysed by the Consulting Chemist during the past month had been submitted.

A letter had been received from the Ministry of Agriculture stating that the personnel of the proposed Departmental Committee on the Fertilisers and Feeding Stuffs Act was under consideration, and that an announcement on the subject would be made shortly. A further letter had been received from the Ministry, asking for copies of any report embodying any conclusions that had been arrived at by the Conference of representatives of the Society with other bodies. It had been left to the Chairman and Dr. Voelker to draw up a report for submission to the Ministry.

Dr. Voelker had reported to the Committee regarding various matters arising out of his correspondence.

## BOTANICAL AND ZOOLOGICAL.

Mr. Plumpton, in the unavoidable absence of Mr. Colman-Rogers (Chairman), presented the following Reports that had been made to the Committee by the Botanist (Professor R. H. Biffen, F.R.S.), and the Zoologist (Mr. Cecil Warburton, M.A.).

## RESEARCH.

*Manuring of Pasture Land.*—An interim report was received on the experiments initiated in Leicestershire on the effect of basic slag and other fertilisers on pasture land as measured by the increase in weight of cattle and sheep. The ground has been prepared and fenced into plots and water supplied. The stock was placed on the plots on May 31, and the first year's control experiment, during which no fertilisers are to be used, has thus been begun.

*Ensilage.*—Experiments have been arranged under the superintendence of Mr. A. Amos, of Cambridge, on the value of silage as food for dairy cows, and its effect on the yield and quantity of the milk. Not every farmer has, or can afford to build, a tower silo, and Mr. Amos is going to preserve the silage in clamps—pits in the ground, in which the fodder is compressed and covered with earth.

Another related research is to be carried out by Mr. Oldershaw in East Suffolk. Tower ensilage will be made this summer and fed to dairy cows next winter to test how far the protein contents of silage can be used to save expensive cakes, the deficiency in carbohydrates being balanced by other foods, such as oats or barley or molasses.

It was resolved that £100 be devoted to these experiments.

#### MINERALOGICAL SOCIETY.

TUESDAY, JUNE 19.

Papers received:—

DR. L. J. SPENCER (with chemical analyses by E. D. Mountain): *New Lead-Copper Minerals from the Mendip Hills (Somerset)*.

DR. W. F. P. McLINTOCK: *On a Petalite-bearing Rock from Devonshire*.

MESSRS. A. BRAMMALL and H. F. HARWOOD: *Dartmoor Granite: Monazite and other accessory Minerals; tourmalinisation*.

SEITARO TSUBOI: *Optical Dispersion of three Intermediate Plagioclases*.

SEITARO TSUBOI: *A Method of Determining Plagioclases in Fine Grains*.

C. S. GARNETT: *The toadstone clays of Derbyshire*.

DR. G. T. PRIOR: *On the Meteoric Stone which fell at Ashdon, Essex, on March 9, 1923*.

DR. G. T. PRIOR: *The Sinai Meteorite*.

#### LIVINGSTONE COLLEGE COMMEMORATION DAY.

A very successful commemoration day was held at Livingstone College on June 13. The chair was taken by Sir Leonard Rogers, C.I.E., F.R.S.

Short statements were made by the Principal, Dr. Tom Jays, and the Treasurer, Mr. R. L. Barclay, as to the work of the past year, and the financial and general position of the College.

#### SOCIETY OF GLASS TECHNOLOGY.

A meeting was held at the Leeds Institute, on Wednesday, June 20. The following papers were received and discussed:—

*Specifications in the Glass Industry*, by PROF. W. E. S. TURNER, D.Sc.

*Notes on the Design of Pot Arches*, by TH. TEISEN, B.Sc.

*Notes on the Ashley Bottle Machine*, by S. ENGLISH, M.Sc.

*The Effect of Titania on the Properties of Glass*, by A. R. SHEEN and PROF. W. E. S. TURNER.

#### INDUSTRIAL PHYSICAL RESEARCH IN AMERICA.

In his recent Presidential Address to the Institute of Physics, Sir J. J. Thomson gave some account of the work he had seen during his recent visit to America in the research departments of some of the great manufacturing firms. These laboratories were established in the face of considerable opposition, but now the universal opinion appears to be that the research department is one of the most profitable in manufacturing concerns, and however great the necessity for economy its cost would be the last to be reduced.

The scale of these laboratories was far greater than anything we have in this country, and much of the work carried out is not merely what might be called development work, but is fundamental scientific work, worthy of a university laboratory.

On the other hand the American universities do not seem designed to produce a large number of men qualified to take up advanced research work. For example, few of the science students have the necessary equipment in mathematics and the stern training which a good Honours man in a great English university has to go through appears to be unknown. The system is doubtless good for the average man, but a successful research institute requires something more than the average man; it needs men with high scientific knowledge. In this regard this country has a distinct advantage we shall sorely need if we are to hold our own in competition.

#### NOTICES OF BOOKS.

*The Manufacture of Acids and Alkalis*, by GEORGE LUNGE, completely revised and rewritten under the Editorship of ALEXANDER CHARLES CUMMING, D.Sc., F.I.C.: Volume I.—*Raw Materials for the Manufacture of Sulphuric Acid and Sulphur Dioxide*, by WILFRID WYLD. Pp.

XIII. + 558. London: Gurney & Jackson, 33, Paternoster Row, E.C. 1923. Price 36s. net.

Prof. Lunge's *Sulphuric Acid and Alkali* first appeared in 1879. The last edition, for which he was still responsible, was published in 1913. In the meantime the progress in chemical industry has necessitated various revisions and much extension. Much of the earlier editions is naturally now obsolete, and even the security of old-established Lead Chamber process is seriously threatened by the newer Catalytic processes.

The present edition, dealing with the heavy chemical industry, has been based upon a very thorough revision of the older work. Much new matter has been introduced, more particularly concerning the by-products, which have lately assumed increasing importance. Illustrations and descriptions of new plant have also been introduced.

Perhaps the most useful parts of this volume are those dealing with the properties and technical analyses of the oxides of sulphur, and the detailed account of the various types of natural and recovered sulphur used in the heavy chemical industry.

Volume V.—*The Manufacture of Hydrochloric Acid and Salt Cake*, by ALEXANDER CHARLES CUMMING, D.Sc., F.I.C. Pp. XV. + 423. Price 31s. 6d. net.

In this volume, the numerous industrial methods for making salt cake and also hydrochloric acid are given in adequate detail. Early chapters describe the raw materials. The chapter on the manufacture of salt cake and hydrochloric acid is naturally the longest, but there is much of importance to industrialists in the accounts of various processes for making sodium sulphate as the main product from salt. This is also true of the chapter dealing with this substance as a by-product.

The Hargreaves process, which has been the subject of so many patents, is still described in good detail, although it is recognised that such old processes are rapidly being superseded.

The later chapters on the winning of hydrochloric acid are largely taken up with the mechanical and absorbing arrangements of the plant.

The constantly increasing over-production of electrolytic chlorine has led to this element being combined with hydrogen, either directly or by interaction with steam.

The account of these methods should prove very instructive to those for whom these treatises have been compiled. Doubtless when a new edition of this highly important work is issued, this section will need to be enlarged with more detail.

The other volumes of this revised edition will be awaited with interest by industrial and technical chemists.

#### BOOKS RECEIVED.

*The Constitution of Matter*, by MAX BORN, translated by E. W. BLAIR, D.I.C., B.Sc., and T. S. WHEELER, B.Sc., A.R.C.Sc.I. Pp. VII. + 80. 1923. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C.2. 6s. net.

*Alcoholic Fermentation*, by ARTHUR HARDEN, Ph.D., D.Sc., F.R.S. Pp. 194. Third Edition. 1923. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 6s. 6d. net.

*Practical Bacteriology for Chemical Students*, by DAVID ELLIS, Ph.D., D.Sc., F.R.S.E. Pp. VIII. + 136. 1923. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 4s. 6d. net.

*Chemistry, Inorganic and Organic, with Experiments*, by CHARLES LOUDON BLOXAM. Pp. IX. + 832. Eleventh Edition. 1923. Messrs. J. & A. Churchill, 7, Great Marlborough Street, W.1. 36s. net.

#### PUBLICATIONS RECEIVED.

In the Bulletin No. 211, published by the U.S. Dept. of the Interior (Bureau of Mines), entitled *The Chloride Volatilisation Process of Ore Treatment*, by THOMAS VARLEY, E. P. BARRETT, C. C. STEVENSON, and R. H. BRADFORD, it is pointed out that the art of treating ores by the chloride volatilisation process is still in the experimental stage. The process has not yet been sufficiently developed along metallurgical lines to warrant a definite statement as to the exact place it will occupy in the industry. The basic theory of the process has attracted the attention of prominent metallurgists, and considerable research and experimental work has been accomplished.

Much of the experimental work done has not been published; but if the accumulated results were made known, they would greatly aid the further development of the process. The bulletin aims to bring the salient features of the process to the attention of metallurgists for the purpose of furnishing information to and receiving comments from interested parties with the ultimate hope that the process will be a commercial success.

If commercially utilised, the process will fill a long-felt want in metallurgy, especially in the treatment of oxidised and semi-oxidised or "carbonate" ores of copper, lead, and silver. Such ores are difficult to treat by gravity concentration or by flotation; in the former their tendency to slime upon crushing and their being of lower specific gravity than the sulphide minerals cause serious losses; in the latter much has been done in sulphidising oxidised ores and subsequently recovering the artificial sulphides by flotation. Difficulties in proper sulphidising and the low recoveries obtained have not balanced the cost of the treatment in many plants, and in very few has it proved successful.

Evidently there is a big void to fill in the treatment of these ores. No radical changes in present methods are forecast, but it is obvious that chloride volatilisation can have a distinct place as a method of treatment for ores that are not readily amenable to present methods. In many plants it might replace concentration methods, especially where part of the mineral content in the ores exists in forms other than sulphides.

In addition to the minerals named above, gold in ores has been readily volatilised. Zinc does not form a volatile chloride, if an oxidising condition is maintained in the roasting operations. Some excellent results have been obtained with carbonate-zinc concentrates containing silver and lead. Practically all the silver and lead were volatilised, but very little of the zinc. Experiments have proved that the process is probably one of the best for making a clean-cut separation of lead and zinc.

Not much work has been done on sulphide ores, because the need is pressing for a volatilising method for treating oxidised and carbonate ores. Experiments on sulphides have been, however, encouraging. When the sulphur content is above 5 per cent. a preliminary roast is usually necessary before chloride roasting and volatilisation.

The effect of sulphur is discussed by Croasdale in his chapter on the history of

the process. He and other investigators declare that sulphur is a consumer of salt, and when it is present in an ore in excessive amounts a proportionately larger amount of salt is required to effect the chloridisation and volatilisation of the metals present.

The process would doubtless be favourable for use in regions not well supplied with water. All the apparatus required for the construction of a plant are practically standard mechanical devices and machinery. The most important raw materials in the operation of a plant are the fuel and the salt or other haloid. In mining districts remote from railroads these materials, of course, would be the largest factor in the cost of running a plant. Nevertheless, the cost would often be more than offset by the freight charges on the concentrates and other supplies necessary for a plant using almost any other kind of process. These conditions will be discussed in some detail in describing the operations of plants that have been built.

The experiments described cover part of the investigations carried on by the U.S. Bureau of Mines on ores from all parts of the United States. Large quantities of different types of ores not amenable to any other process were available, and the method developed gives promise of great commercial importance.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Abstract Published this Week.*

195849—Cellulose acetate solutions and compositions; celluloid; films; varnishes.—British Cellulose & Chemical Manufacturing Co., Ltd., 8, Waterloo Place, London; Bader, W., and Dickie, W. A., British Cellulose & Chemical Manufacturing Co. Works, Spondon, near Derby.

Celluloid-like products, plastic masses, films, varnishes, solutions and other preparations and compositions having a basis of cellulose acetate, are prepared with the employment of tri-chlor tertiary butyl alcohol as solvent or plastifier; celluloid prepared in this manner is tough, elastic and non-inflammable. According to the use, volatile or other solvents, diluents, plastifiers, filling materials, colouring matters, &c., may be added. In examples, celluloids are prepared with the aid of the tri-chlor tertiary butyl alcohol with or without the addition of triphenyl phosphate or castor oil; films, using a solution to which acetone has been added; and a varnish, with the addition of acetone or methyl acetate.

Messrs. Rayner & Co. will obtain printed copies of the published specifications only, and forward on post free for the price of 1s. 6d. each



# THE CHEMICAL NEWS,

VOL. CXXVI. No. 3298.

## NOTE UPON THE PROPERTIES OF MUSCARINE.

BY JOHN MISSENDEN, B.Sc.

*Muscarine*, which is a content product of a number of poisonous fungi (notably the *Amanita muscaria*), has the formula  $C_5H_{13}O_3N$ , but its constitution is unknown. Formerly, it was believed to be a choline oxy-substitution product. Schmiedeberg and Harnack,<sup>1</sup> in their reaction with choline and nitric acid, gave the base obtained (which they believed to be muscarine) as  $OHN.(CH_3)_3.CH_2CH(OH)_2$ . The arguments of both Berlinerblau<sup>2</sup> and Boehm<sup>3</sup>, however, very conclusively show that this base possesses neither the properties nor constitution of muscarine, the conclusions being the outcome of careful comparison with the natural product. At the same time, until more is known of the subject, the synthetic product may be accepted as a choline ester of the constitution  $OHN.(CH_3)_3.CH_2.CH_2ONO$ . Natural muscarine, we believe, possesses a totally different constitution; i.e.,  $NO.CH_2.(CH_3)_2.CH_2.CH_2.NO.OH$ , although there is some doubt as to the exact placement of the initial nitrosyl group.

Natural muscarine is certainly not a choline ester, inasmuch that its solutions are not decomposed by boiling in acid and alkaline solutions. Discussions upon the matter were reported by Weinbagen.<sup>4</sup> It is worth noting that the physiological action of muscarine resembles that of acetyl-choline.

<sup>1</sup> *Arch. ex. Path. Pharm.*, 1877, VI., 101.

<sup>2</sup> *Ber. Deut.*, 1884, XVII., 1141.

<sup>3</sup> *Arch. ex. Path. Pharm.*, 1885, XIX., 187.

<sup>4</sup> *Journ. Amer. Chem. Soc.*, 1920, XLII., 1670.

## DISTRIBUTION OF INSECTICIDE BY AEROPLANE.

Mr. R. O. Wahl, Lecturer in Entomology in South Africa, who recently returned to that country from America, reports that when visiting the State Experiment Station at Wooster, Ohio, during last year, his attention was drawn to an experiment carried out by that Experiment Station and the City of Cleveland, in co-operation with the United States Air Service, in combating an outbreak of the catalpa sphinx (*Ceratomia catalpas*, Bvd.) in a catalpa grove by distributing the insecticide from an aeroplane. Through the courtesy of the officers conducting the experiment it was possible for Mr. Wahl to take an active part in the work, seeing the dusting from the ground and the air, and in assisting in checking the results immediately after the dusting after a lapse of 24 hours and again a week later. The section of the wood sprayed was a dense grove containing trees of different kinds, elm, spruce, maple, etc., and varying in size from 60 ft. down. There was considerable thick undergrowth as well as much bracken and large plantings of rhododendrons. The penetration of the dust was remarkable and the killing very successful. Unfortunately, a heavy thunderstorm and torrential downpour occurred a few hours after the completion of the dusting and robbed it of much of its value. A portion was redusted the following day, resulting in a practically total killing of the caterpillars.

Much more experimental work is necessary, but a new field of investigation in this direction is opened to the entomologist and other scientists and one that appears to have great possibilities.

## MACHINERY FOR PHARMACEUTICAL PREPARATIONS REQUIRED IN AUSTRALIA.

Mr. S. W. B. McGregor, --M. Senior Trade Commissioner in Australia, reports that a Melbourne firm of manufacturing chemists specialising in the production of galenicals and other pharmaceutical preparations, are desirous of receiving particulars from British manufacturers of any machinery, appliance, apparatus, etc., used in the manufacture of such products in a wholesale way, such as percolators

(mechanical and otherwise), evaporators, boiling pans, filters (*not* water filters). They are particularly interested in any plant that would be of service in the manufacture of extract of glycyrrhizæ and extract of cascara on a large scale.

The firm are understood to be of good repute and standing.

British firms interested in this enquiry can obtain the name and address of the enquirers upon application to the Department of Overseas Trade (Room 52), 35, Old Queen Street, S.W.1.

### GERMANY'S TRADE AND INDUSTRY IN MAY.

Mr. F. Thelwall, Commercial Secretary at Berlin, has forwarded to the Department of Overseas Trade information on German trade and industry during May.

In spite of the unfavourable general situation, there was a not inconsiderable improvement in business in many branches of industry. The special feature in trade was the rise of the dollar, which again led to an increased desire to purchase on the part of inland customers, while foreign sales improved in consequence of the greater span between prices and of the easier export conditions. German industry also benefited by the altered conditions, although its outlook for the future continues melancholy. New difficulties arose in procuring British coal, the import of which, owing to the depreciation of the mark, had, of course, to be restricted. The coal stocks had, therefore, to be broken into to a larger extent. In occupied territory the strike did not greatly affect the industrial situation. In unoccupied Germany also, as a result of the rise in prices amounting to 33.8 per cent. as compared with April, new wage demands were made.

#### *Mining.*

The coal position of industry in occupied territory continued to depend on the measures of the occupying Powers. Many cokeries ceased work. Most pits only produced sufficient coal to meet the needs of their own foundries. In many cases transport between the foundries and the pits has been interrupted by the occupying Powers. The price of coal was raised to 143.510 marks per ton.

In the potash industry, inland trade had at first still to suffer from considerable

difficulties. The freight reductions for the summer introduced by the German Potash Syndicate led, however, to a substantial improvement of sales in the second half of May. By the summer reductions, the potash industry gave agriculture, as in the previous year, the opportunity of covering during the summer months a considerable portion of its autumn requirements at reduced freights. Foreign business also became lively on the renewed depreciation of the mark and exportation took place, particularly to America. Alsatian competition made itself increasingly felt in foreign trade. Coal deliveries left nothing to be desired.

#### *Electro-Technical Industry.*

Measuring instruments found a good market, and business activity in the high-pressure current industry increased.

#### *Chemical Industry.*

The chemical preparations industry still suffered at the beginning of the month under the prevailing disinclination to buy. On the rise of the dollar, business revived on a continually increasing scale. Many orders from abroad were also received, so that at present the degree of employment is comparatively favourable. Practically no benefit accrued to the works from the new export facilities, as the reduction of the export duty did not go nearly far enough. In the sheet glass industry, exports at first declined ~~under~~ compared with the preceding month; then, as a result of the fall of the mark, a considerable demand from abroad set in. Exportation to Italy, Reval, and also to America and Africa took place from accumulated stocks.

In the hollow glass industry the supply of raw materials and of coal was adequate; soda deliveries improved. Work for stock had in part to be done. In the case of some special articles a slight improvement of sale conditions was reported.

#### *Indiarubber.*

Conditions in the indiarubber industry much improved as a result of the further depreciation of the mark. Fearing a further rise of foreign values, consumers sought to cover their requirements anew and to effect substantial purchases which presumably did not correspond with the actual consumption.

## GENERAL NOTES.

## DIE CASTING RESEARCH.

## AIDS TO MASS PRODUCTION.

The British Non-Ferrous Metals Research Association has undertaken an extensive series of investigations on Die Casting Alloys which will spread over at least three years, and entail an expenditure exceeding £10,000. Full particulars of the scheme can be obtained from the Association's headquarters, 71, Temple Row, Birmingham.

The development and support of die casting in this country as a means of rapid production, is recognised as of great national importance both for ordinary commercial production, in the most diverse industries, as also for munitions and equipment of the fighting services.

The Department of Scientific and Industrial Research, after holding conferences of those interested in die castings, has promised most substantial financial support to the research. The Research Associations of the British Motor and Allied Industries, of the Scientific Instruments, and of the Electrical and Allied Industries have also afforded their support, and are represented on the Committee controlling the investigations. It remains for the industry—makers and users—to provide their quota of the fund required, as without this it will be impossible to fully develop the work, the results of which will be primarily available to those who support the research.

Since die castings serve chiefly as components of plant and machinery, it is not always recognised how important they are, but anyone enquiring into the subject will come across very varied uses in the automobile industry, and such applications as brush gear of electrical machinery, gas meter parts, vacuum cleaner fittings, etc., etc.

Sooner or later, almost every branch of industry in which metal parts of any complicated shape are required, turns to die castings as the ideal for economical production. The sphere of application will extend considerably if the research work contemplated succeeds in improving the quality and assuring the reliability of the alloys used.

Various types of alloys are used in die casting, and recognising the wide field, the proposed research has been divided into

three sections: 1, Brass and Bronze Alloys; 2, Aluminium Alloys; 3, Low Melting Point Alloys (Zinc, Tin, Lead, etc.). These three branches, with suitable arrangements for co-operation, will be dealt with in separate institutions, under the supervision of recognised leaders of metallurgical research.

Every care is being taken in the constitution of the Committee which controls the work, to ensure that both the manufacturers and the users are represented.

Work of this nature demands the close interest of the industry, and it is hoped that no difficulty will be experienced in obtaining the small subscriptions required to assure the substantial Government support, which is only available in a measure dependent on the backing of the scheme by the industry.

PHYSICAL AND CHEMICAL SURVEY  
OF THE NATIONAL COAL  
RESOURCES.

One of the main functions of the Fuel Research Board is a survey and classification of the coal seams in the various mining districts by means of chemical and physical tests in the laboratory, supplemented where desirable by large scale tests at H.M. Fuel Research Station, East Greenwich, or elsewhere. The Board consider that the best way to carry out this work is by means of local committees, the personnel of which would include colliery owners, managers, representatives of the Fuel Research Board, and of the Geological Survey of Great Britain, as well as of outside scientific interests. Each committee would be charged with the duty of superintending the work of the survey in a coal mining area; and in this way the survey would become, from the commencement, of practical value, since local knowledge and experience would be made available, and the selection of seams would be decided by those most likely to estimate correctly the relative importance of the problems to be solved. The seams selected would undergo physical and chemical examination by the local experts, after which a final selection would be made of those likely to justify experiments on a practical scale to test their suitability for particular uses or methods of treatment.

The first of these committees has now

been actively at work in the Lancashire and Cheshire area for nearly eighteen months, and the Board have recently appointed a committee to deal with the survey in the South Yorkshire area. The South Yorkshire Coal Trade Association and the Midland Institute of Mining, Civil and Mechanical Engineers are co-operating in the work. The composition of the committee is as follows:—

Mr. J. Brass, Mr. Robert Clive (hon. secretary) and Mr. H. Danby—representing the South Yorkshire Coal Trade Association.

Lieut.-Col. H. Rhodes, M.Inst.C.E., M.I.Min.E., F.S.I.—representing the Midland Institute of Mining, Civil and Mechanical Engineers.

Prof. R. V. Wheeler, D.Sc.

Mr. C. H. Lander, D.Sc., M.I.Mech.E., A.M.Inst.C.E., Director of Fuel Research (Chairman *pro tem*)—representing the Fuel Research Board.

Mr. Walcot Gibson, D.Sc.—representing the Geological Survey of Great Britain.

The Federation of British Industries has issued an interim report on inter-Imperial trade.

The report does not cover every aspect of inter-Imperial trade, and the Federation propose, at a later date, to address one or more further reports to the Government, dealing with the questions which are not dealt with in the present report.

In the Federation's opinion, the fullest possible development of inter-Imperial trade is essential in the interests of the Empire as a whole, both for economic, political and social reasons. The problem should be approached not merely from the point of view of the advantages likely to accrue to Great Britain, but from the point of view of mutual advantage to all parts of the Empire.

#### FINE GLASS IN THE MANSARD GALLERY.

An extremely interesting exhibition of fine glass has recently been opened at the Mansard Gallery, 196, Tottenham Court Road, London, W.1.

Carefully selected from a number of countries, the play of light on the varied colours and textures gives an atmosphere of fairy-

land. Light shapes in clouded topaz and smoke grey come from Sweden. Sea green and pale amethyst fantasies of the Venetians contrast with the deep richness of our own Old Bristol blue and puce. Limpid crystal from the old Whitefriars works, and the sturdy cut table glass from Edinburgh reflect in their facets the shimmer of Czecho-Slovakia's amber lustre and the orange glow of bowls from France. The consummate artists of Murano have sent a few pieces flecked with gold, while a table set with iridescent glass from Holland holds all the glories of a bubble in the sun. The revival of industries in Palestine is shown by some characteristic peacock blue glass from Hebron.

Alongside these contributions from far lands are tables laid with simple, well-shaped wine-glasses and tumblers in plain crystal; practical and graceful vases for flowers, and larger ones for tall spikes of delphiniums or spreading boughs. A collector's piece is the tall engraved goblet made to commemorate the Armistice, bearing the appropriate inscription: *Dominus loquitur—arma silent*, and dated the eleventh hour of the eleventh day of the eleventh month, 1918.

The revival of the prismatic lustre glass for electric lighting is particularly happy. A series of these lustre light pendants and wall brackets will be of particular interest to architects.

The exhibition, which has been organised by Messrs. Heal and Sons, of Tottenham Court Road, is being held during the present and the next month. Admission is free. —*The Board of Trade Journal.*

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL SOCIETY.

THURSDAY, JUNE 28.

Paper read:—

PROF. V. H. BLACKMAN, F.R.S., A. T. LEGG, and F. G. GREGORY. *The Effect of a Direct Electric Current of very Low Intensity on the Rate of Growth of the Coleoptile of Barley.*

Papers read in title only:—

MISS R. M. TUPPER-CAREY and PROF. J.

H. PRIESTLEY. *The Composition of the Cell Wall at the Apical Meristem of Stem and Root.* Communicated by Dr. F. F. Blackman, F.R.S.

L. J. HARRIS. *The Titration of Amino- and Carbozyl Groups in Amino-Acids, Polypeptides, etc.* Communicated by Prof. F. G. Hopkins, F.R.S.

DR. M. S. PEMBREY, F.R.S., N. W. MACKEITH, W. R. SPURRELL, E. C. WARNER, and H. J. WESTLAKE. *Observations on the Adjustment of the Human Body to Muscular Work.*

F. A. E. CREW. *Studies in Intersexuality. II.—Sex-reversal in the Fowl.* Communicated by Prof. R. C. Punnett, F.R.S.

PROF. W. FINKLER. *Analytical Studies on the Factors causing the Sexual Display in the Mountain Newt (Triton alpestris).* Communicated by Prof. E. W. MacBride, F.R.S.

G. A. SCHOTT, F.R.S. *On the Scattering of X and  $\gamma$  Rays by Rings of Electrons—The Effect of Damping of the Incident Radiation.*

MAJOR P. A. MACMAHON, F.R.S. *On a Class of Transcendents of which the Bessel Functions are a Particular Case.*

L. C. MARTIN, D.Sc. *The Photometric Matching Field.* Communicated by Prof. H. L. Callendar, F.R.S.

G. P. THOMSON. *Test of a Theory of Radiation.* Communicated by Sir Joseph Thomson, F.R.S.

A. LL. HUGHES, D.Sc., and P. LOWE. *Intensities in the Helium Spectrum.* Communicated by Prof. H. A. Wilson, F.R.S.

A. A. DEE. *The Effect of Quenching from above the Carbide Transition Temperature upon the Magnetism of Steel.* Communicated by Prof. S. W. J. Smith.

T. S. P. STRANGEWAYS and H. E. H. OAKLEY. *The Immediate Changes observed in Tissue Cells after exposure to Soft X-Rays while growing "in vitro."* Communicated by W. B. Hardy, Sec. R.S.

THURSDAY, JUNE 21.

CROONIAN LECTURE, by F. F. BLACKMAN, F.R.S. *The Problems of Plant Respiration considered as a Catalytic Process.*

In recent years much progress has been made in analysing the complex series of molecular changes that are summarised in the crude equation of respiration,  $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$ , and it is clear that catalytic enzymes of protoplasm are the specific agents determining the sequence and magnitude of these changes.

In this lecture an attempt is made to face the other aspect of respiration, which is peculiarly the problem of plant physiologists. This is the problem of the meaning of the varying intensity of respiration as shown in different nutritional states of activity of the same cell, in the different phases of dormancy, development and senescence, and in experimental conditions which lie outside natural experience.

Our knowledge of this wide subject is fragmentary, but a useful purpose should be served, for future research, by an attempt to examine these variations of respiratory intensity in terms of the factors which are known to affect the rate of activity of catalytic processes of the type studied *in vitro* as enzyme catalysis. These factors are (1) the amount of the catalytic agent, (2) the concentration of the substrate acted upon, (3) the presence of depressant substances which reduce the effective surface of the catalyst, (4) the influence of end products of activity as depressants of a similar nature, (5) hydrogen ion concentration controlling the dissociation of these amphoteric enzyme catalysts, and (6) dehydrating agents affecting the imbibition and water relations of the catalyst.

A complete formulation of biological variations of respiration in these physico-chemical terms is an ultimate goal of plant physiology; at present we are only at the beginning, determining the orientation of future researches.

The problem that may first be considered in some detail is the problem of the relation of respiration intensity of a cell to the concentration of the substrate, hexose sugar. Several isolated sets of data, bearing on this, are available. With plants in their natural existence this relation is intimately linked with another relation—that of the hydrolysis of starch to supply the substrate sugar or respiration. This is illustrated by

the starch-sugar balance of the cell and its significant variations with temperature.

In certain natural dormant conditions of vegetative organs, such as tubers, and in artificial starvation of active tissues, the concentration of hexose may be reduced apparently to zero. Respiration does not then cease, but is maintained at a certain definite minimal value. At this phase respiration passes out of its normal position of being merely the end link in a chain of floating carbohydrate catabolism, beneficially supplying energy for the service of metabolism, and becomes a devastating force. Lacking the "protection" of carbohydrates, nitrogenous substances now undergo oxidation; in this way the actual texture of protoplasm seems ultimately to be destroyed, and the end of vital organisation takes the form of sudden failure of the semi-permeability of the protoplast.

Variations of catalytic activity, by steady seasonal drift, characterise the life-history of individual plant organs. These are most marked in the phases of early development, of dormancy, and of senescence; here the experimenter has to face the difficulty that the essential efficiency of respiration may, under constant conditions, not be absolutely the same on any two successive days. Some of these phenomena can be referred to variations in the amount of catalytic agent, others may be due to the presence of depressants.

Variations of respiratory intensity may also be brought about by the accumulation of the end product, carbon dioxide, acting as a depressant of respiration. The quantitative relations indicate that carbon dioxide unites with the catalyst and lowers its effective activity, unless it can escape adequately by diffusion.

The whole of the relations of the catalytic system of plant respiration outlined above deal with normal conditions in which adequate oxygen concentration is maintained at the active centres. With inadequate oxygen the molecular sequence of changes undergone by sugar is deflected and there is set up a new system of relations, those of anaerobic respiration, which are at present also being explored quantitatively.

#### THE GEOLOGICAL SOCIETY OF LONDON.

JUNE 6.

The following communications were read:—

*On a New Blattoid Wing from the Harrow Hill Mine, Drybrook (Forest of Dean)*, by HERBERT BOLTON, D.Sc., F.R.S.E., F.G.S.

The author describes a new type of fossil insect-wing found in shale on the waste-heap at the Harrow Hill Mine, and since recognised as being derived from the roof of the Coleford High Delf Seam. The specimen was discovered by students of the Imperial College of Science and Technology in the summer excursion of 1921.

*Contact-Metamorphism in the Comrie Area of the Perthshire Highlands*, by CECIL EDGAR TILLEY, PH.D., B.Sc., F.G.S.

Lantern-slides, etc., were exhibited by Dr. H. Bolton; and rock-specimens, microscope-sections, and lantern-slides were exhibited by Dr. C. E. Tilley, in illustration of their respective papers.

A meeting of the Society was held on June 20, when Dr. Herbert H. Thomas, M.A., V.P.G.S., gave a demonstration on "The Source of Origin of the Stones of Stonehenge."

The following communications were read:—

*The River-Gravels of the Oxford District*, by KENNETH STUART SANDFORD, B.A., F.G.S.

*The Deposits of Paleocene Mammalia in Belgium*, by PROF. LOUIS DOLLO, Sc.D., FOR.MEM.G.S., and PROF. P. TEILHARD DE CHARDIN, D.Sc.

#### PHYSICAL SOCIETY OF LONDON.

A meeting of the Society was held on Friday, June 22.

A lecture, entitled *The Excitation and Ionization Potentials of Gases and Vapours*, was delivered by PROF. F. HORTON, M.A., D.Sc., F.R.S., Royal Holloway College, University of London.

Proceedings at the meeting held on June 8, Alexander Russell, M.A., D.Sc., in the chair.

PROF. JAMES G. GRAY, D.Sc., F.R.S.E., Cargill Professor of Applied Physics in the University of Glasgow, delivered a lecture, entitled *A General Solution of the Problem*

of *Finding the True Vertical for all Types of Marine and Aerial Craft*. The lecture was accompanied by demonstrations with gyroscopes.

In the first part of the lecture it was shown that the difficulties presented by this problem arise from the horizontal accelerations which result from the turning of vehicles. A gyroscopic pendulum to succeed must possess a real precessional period, or a virtual precessional period during turning motion of the vehicle on which it is mounted, which is measured in hours.

Pioneer forms of Gray stabiliser were described. These were devised by the author and his brother for use in the Royal Naval Air Service. A system composed of a single gyroscope (mounted with its axis normally vertical) and an erector connected rigidly to one another, is pivoted to a gimbal frame by means of two cross pivots; and this frame is in turn attached by means of fore and aft pivots to uprights, or the equivalent, carried by the aeroplane. The system composed of the gyroscope and erector is mounted and balanced up so that the centre of gravity of the entire system coincides with the intersection of the pivot axes.

Various forms of erector made use of with these pioneer instruments were described, and their dynamical action discussed. One form consists of a circular track carried by the pivoted system, and so arranged that when the pivoted system is upright the track is horizontal. One, two, or more balls rotate on the track, each controlled by a pusher and a check carried by a member which rotates slowly (about 12 revolutions per minute) in the direction of spin of the gyroscope. When the system is upright the balls move round the track in contact with their pushers, and form a balanced system. When the system is inclined to the vertical the track is inclined to the horizontal, and each ball when ascending the slope of the track rests against its pusher, but after crossing the crest of the slope it is accelerated down the track and rests against its check. The motion of the balls relative to the pushers and checks results in the application to the pivoted system of an integral erecting couple.

It was shown how the contrivance could be arranged so that the stabiliser possessed the property that it was blind to the apparent vertical during turning motion of an aeroplane on which it was mounted, but

conscious (so to speak) of the true vertical during the ordinary flight of the aeroplane.

These pioneer forms of the instrument were found to possess an accuracy, for bombing purposes, amounting to one-eighth or one-tenth of a degree, or about 20 feet on the ground from a height of 12,000 feet.

Previous work on the problem failed because the devices produced possessed the property that they left the true vertical quickly in the presence of the accelerations which accompany turning motions of the aeroplane, and returned to the true vertical only very slowly after the resumption of ordinary flight. The pioneer forms of Gray stabiliser (when properly used) moved only very slowly, if at all, towards the apparent vertical when the aeroplane was turning, and after the resumption of ordinary flight moved towards the true vertical (supposing an error to exist) relatively quickly.

Finally the latest forms of Gray stabiliser were described. These set themselves into the true vertical even when the vehicles on which they are mounted are turning, and this holds for all speeds of turning. Control is never lost. This result is obtained by constructing the apparatus so that a horizontal component of spin lies across the pivoted system, that is, parallel to the cross pivots. The pivoted system is mounted so as to be pendulous with respect to the pivots, and the direction of the horizontal spin, and its amount, is arranged so that when the vehicle turns there comes into existence a gyroscopic couple, applied about the fore and aft pivots, which is exactly equal and opposite to the so-called centrifugal couple applied to the pivoted system. Both couples are proportional to the angular speed at which the vehicle turns, and both change sign with that of the turning motion. Hence the compensation is correct for all speeds of turning.

This type of stabiliser, when fitted with special erectors, a simple example of which was described, supplies a complete solution of the vertical problem. Assuming an error made (small) in adjusting the compensating component of spin the resting position of the device is one in which it is inclined to the true vertical at a very small angle. The devices solve the problem completely for the rapid and slow turning movements of aeroplanes, and for the turning motions of ships.

#### DISCUSSION.

Sir James Henderson, after compliment-

ing Professor Gray on his lecture, referred to the great difficulties of the problem. These difficulties vary with the accuracy aimed at. If it be only required to maintain the vertical within one degree the problem is very easy, but if it be required to maintain it within one minute of arc the difficulties are very great, almost if not quite unsurmountable. The difficulties increase almost as the square of the accuracy aimed at.

Professor Gray had concentrated upon the problem of the bomb-dropping sight for aircraft, and had achieved considerable success during the war. The practical accuracy then aimed at in this connection was to maintain the vertical to about  $\frac{1}{4}$  degree, and to this degree of accuracy Professor Gray had attained, as stated in his lecture.

The accuracy of any instrument of this type could be calculated accurately if the method of control were continuous. In Professor Gray's instrument the method of control involves a discontinuity which does not lend itself to easy computation. There are other methods of control, however, which are continuous and which enable accurate calculations to be made.

Professor Gray had said nothing in his lecture to give any idea of the amount of damping he employed. This determines the accuracy, because if the damping be very great the gyro follows the *virtual* vertical at corresponding rates and the deviation increases accordingly. On the other hand, if the damping be greatly diminished a considerable deviation arises from the rotation of the earth and a connection to the gyro-compass is required to compensate it. Thus when great accuracy is required the problem becomes excessively difficult.

Professor Gray's method of eliminating the effects of the centrifugal force during a turn was ingenious. If the speed adjustment be perfect, then any deviation which the pendulum has relatively to the vertical at the beginning of the turn turns azimuth with the plane. The deviations due to any change of velocity either fore or aft or during a turn are, however, not so easily compensated.

M. Paul Schilowsky said that naval experts ask for a degree of accuracy which must be the despair of gyroscopic inventors, but accuracy to a degree or half a degree of angle is by no means unattainable. He had tried a different solution from that given by the lecturer, viz., that of suspending

the gyroscopic pendulum in neutral equilibrium on knife edges passing through its centre of gravity. In time, however, precession takes place with this arrangement, and the pendulum errs progressively from the true vertical. What is required is that the pendular suspension should be neutral for curved motion but stable for rectilinear motion. Sir James Henderson has designed an instrument for indicating the curvature of the path of the aeroplane. A combination of the two devices should make it possible to meet the requirement mentioned. The lecturer's plan was open to the objection that very rapid changes of rotary speed in the gyroscope would be necessary to compensate for the rapidity with which an aeroplane changes its linear speed. His admiration for the lecturer's work was sincere, and he should expect great results if the latter would take up the problem of altering the suspension of the gyroscope according to the curvature of the path.

Mr. T. Smith said that all present would have followed the lecture with the greatest interest. It was not easy, however, for those less familiar than the lecturer with the practical handling of gyroscopic apparatus to appreciate all the points at issue in the absence of a formal mathematical treatment. Possibly mathematical difficulties would arise from the discontinuities which had been mentioned by Sir James Henderson, but the modern methods for dealing with discontinuous quantities developed in connection with the quantum theory might perhaps give a hint as to the line of attack to be adopted in the present case.

The lecturer, in reply to the discussion, dwelt mainly on the point raised by M. Schilowsky, and claimed that his apparatus did become automatically "blind" during curved motion of the aeroplane in a manner satisfying M. Schilowsky's requirement. The effect of the earth's rotation on the gyroscope is very small provided the precessional period is long.

The President congratulated the lecturer on his solution of an important and difficult problem, and proposed a vote of thanks, which was carried with acclamation.

#### SOCIETY OF GLASS TECHNOLOGY.

The last ordinary meeting of the Society for the session 1922-23 was held in Leeds, on June 20. Prof. W. E. S. Turner, D.Sc., read a paper on "Specifications in the



Glass Industry." He pointed out that certain types of glass, such as that used for optical purposes, were bought on specification, and had to conform strictly to certain properties. In the enormous industry, however, which was concerned in the production of such things as containers for liquids and solids, no one seemed to have attempted to make or even purchase on this basis. Cases had arisen which had emphasised lack of precision. For example, a recent law case was fought round the quality of bottles supplied, and from the evidence it was quite evident that the actual quality of the glass did not seem to have been specified. Several other cases had arisen, pointing to the need of deciding to what specification different glass articles should conform. If the industry was to insist on furnace material makers providing refractories, to specification, then the glass manufacturers must show they were prepared to supply their goods to specification. Prof. Turner dealt with specifications which might be made the working basis for such articles as medicine bottles, beverage bottles, and other types of container.

Mr. TH. TEISEN, B.Sc., contributed *Some Notes on the Design of Pot Arches*, his remarks being illustrated by lantern slides.

Criticising the old type of pot arch, Mr. Teisen said the flue outlet for burnt gases at the back wall near the bottom gave cold pockets inside the furnace. On the other hand, the ensuing lack of proper heat distribution could be somewhat helped by longer soaking. The fire boxes being open, the fire itself was not under proper control.

The Continental type, with direct fired furnace, fire-box below, combustion flues and air flues leading to the uptake at the back of the chamber, and fumes passing through holes in the floor near the front and thence to the chimney, was better but not so practical. With the entry of the gas-fired pot furnace in the glass industry, a demand had arisen for a more modern type for heating pots. That type should contain better facilities for heat distribution and control; it should also combine good conditions for working and firing with easy installation and economy of space. A gas-fired recuperative pot-arch, designed on these lines some years ago, and which proved a success, was described, as well as a pot-arch at Messrs. Moncrieff's, where, during the first stage of burning, a low fire was kept on the grate, fed through the ash door. The secondary air slide was closed,

and the furnace was in other ways directly-fired. For the purpose of driving out natural and combined water without producing surface cracks, water was kept dripping on the firebars, as well as on a plate arranged in front of them, thereby producing a certain amount of steam, which helped to retard a too quick drying of the surface parts and allowed the inside to evaporate its moisture at the same rate as the outside. The steam produced made it necessary to run with the usual density of smoke. That type took up little space with proportionately less building cost, and results in practice were quite satisfactory.

Mr. S. ENGLISH, M.Sc., gave a paper entitled *Notes on the Ashley Bottle Machine*. He remarked that to one familiar only with modern glass forming machines, it might be surprising to hear that the home of bottle making machinery was on this side of the Atlantic, but such was the case, and it was only after the possibility of making narrow mouth bottles satisfactorily by machines had been proved here, that such bottle making machinery was introduced in America. The first machine to make narrow mouth bottles at all satisfactorily was designed and built by H. M. Ashley in Yorkshire. About 1866, Josiah Arnall, postmaster at Ferrybridge, conceived an idea which would enable bottles to be blown by machinery. He submitted his idea to a bottle manufacturer, but apparently it was too crude or too revolutionary. Nearly twenty years later, H. M. Ashley, the manager of an iron foundry near the post office, went to live with Arnall, and there can be no doubt that Arnall discussed with Ashley his ideas concerning the possibility of blowing bottles by machinery.

As a result of such discussion, Ashley built an experimental machine in which glass was poured into an inverted mould, which was fitted with a plug to form the inside of the neck and with a movable top plunger. When a charge of glass had been placed in the mould, the sliding plunger was brought down on top of it, thus pressing it down around the fixed plug and forming the neck. Compressed air was then admitted through the plug, blowing up the bottle and at the same time raising the sliding plunger, to the desired extent. Such an arrangement was very simple, and was naturally unsuccessful, but it had sufficient good points to cause Ashley to try to develop it into a useful machine. The first

step in its improvement appeared to have been an appreciation of the fact that three moulds were necessary, one for forming the neck of the bottle, the second for giving a preliminary form to the main body of the glass, and the third for blowing the finished bottle. This provision of a ring mould, parison mould and blow mould was the foundation on which all Ashley's experimental machines were built, and has been incorporated in every successful machine since.

### MINERALOGICAL SOCIETY.

JUNE 19.

Dr. A. Hutchinson, F.R.S., President, in the chair.

DR. L. J. SPENCER (with chemical analyses by E. D. Mountain): *New copper-lead Minerals from the Mendip Hills (Somerset)*.

Mendipite ( $2\text{PbO} \cdot \text{PbCl}_2$ ), which occurs as crystalline nodules in manganese-ore, is recorded from new localities. *Chloroxiphite* ( $2\text{PbO} \cdot \text{Pb}(\text{OH})_2 \cdot \text{CuCl}_2$ ) as green monoclinic blades resembling epidote, and *Diaboleite* ( $2\text{Pb}(\text{OH})_2 \cdot \text{CuCl}_2$ ) as bright-blue tetragonal plates resembling boleite, both occur embedded in the mendipite. Hydrocerussite ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ) is abundant, sometimes as large crystals (*i.e.*, crystallised "white lead"). Crednerite ( $\text{CuO} \cdot \text{Mn}_2\text{O}_3$ ) forms fan-like aggregates of thin plates. Pyromorphite, which some centuries ago was evidently an important ore of lead in the Mendips, has been preserved (together with mendipite, hydrocerussite, etc.) in the Woodwardian collection (1728) at Cambridge. Wulfenite and mimetite have been found at Higher Pitts, near Priddy. The various minerals show progressive stages of alteration with some well-marked pseudomorphs: mendipite  $\rightarrow$  hydrocerussite  $\rightarrow$  cerussite; chloroxiphite  $\rightarrow$  hydrocerussite + malachite I cerussite + crednerite  $\rightarrow$  malachite II.

W. F. P. McLINTOCK: *On a petalite-bearing Rock from Devonshire*.

The well-known aplite from Meldon, in Devonshire, is shown to have developed in certain parts of the intrusion a soda-lithia phase rich in the rare lithium-aluminium silicate, petalite. This mineral, not previously known from Britain, occurs as one

of the final products of consolidation of the aplite either in coarse-grained veins of pegmatite, associated with quartz, orthoclase, albite, a lithia-bearing mica, tourmaline, and apatite, or as irregularly-shaped masses throughout the rock itself. The petalite gives rise by decomposition to the pink clay, montmorillonite, so well-known from this locality. Certain other veins, free from petalite, are also present, the most interesting constituents of the rarer types being prehnite, axinite and a pleochroic cordierite. The apatite in the aplite is shown to be a pneumatolytic mineral, occurring not only in the rock as ophitic patches enclosing quartz and feldspar, but also impregnating certain xenoliths of peculiar type. Deep-blue crystals developed in the druses of a coarse grained modification of the aplite and associated with pink, yellow, and green tourmaline, are described.

A. BRAMMALL and H. F. HARWOOD: *The accessory Minerals of the Dartmoor Granite*.

The complete list of minerals identified by the authors is as follows: Biotite and muscovite; tourmaline, topaz, fluor; zircon, apatite, monazite, garnet, sphene, and pale amphibole (edenite); ilmenite, magnetite, pyrites, pyrrhotite, and molybdenite; gold and silver; rutile, brookite, anatase, cassiterite, and specular iron ore; barytes and allanite; andalusite, sillimanite, cordierite, spinel, and corundum. Tourmaline originated at two stages in the cooling history of the intrusion: (1) pre-solidification—primary and secondary; (2) post-solidification—secondary. The more severe and widespread pneumatolysis and the lodes are referred to a post-solidification stage.

SEITARO TSUBOI: *Optical dispersion of Three Intermediate Plagioclases*.

The principal refractive indices,  $\alpha$ ,  $\beta$ ,  $\gamma$ , of (1) oligoclase from Hawke Mine, Bakersville, North Carolina; (2) andesine from Maeyama, Shinano, Japan; and (3) labradorite from County Down, Ireland, for light of 9 different wave-lengths (700, 671, 644, 610, 589.3, 554, 535, 527, 508.5 $\mu\mu$ ) were determined. The optical orientations of the first and the third of the above three feldspars, for light of 5 different wave-lengths (700, 644, 589.3, 535, 508.5 $\mu\mu$ ) were also determined.

SEITARO TSUBOI: *A Dispersion Method of Determining Plagioclases in Cleavage-Flakes.*

This new method is based on the principle of H. E. Merwin's improved immersion method. By means of a diagram a quick and exact determination of plagioclases is possible. It is applicable to such small crystals as are common in rocks.

C. S. GARNETT: *The "Toadstone-clays" of Derbyshire.*

The olivine-dolerites ("toadstones") of Derbyshire under two types of alteration: (1) by ordinary weathering to limonite or ochreous deposits; (2) in the absence of oxidising agents under a limestotic covering, they may pass through dolerite-greenstone and "green-earth" to a greenish-white or almost white clay ("toadstone-clay") with the composition  $2Al_2O_3 \cdot 6SiO_2 \cdot 3H_2O$ .

DR. G. T. PRIOR: *The Meteoric Stone which was seen to fall at Ashdon, near Saffron Walden, Essex, on March 9, 1923.*

The stone, which weighed about 1,300 grams, is a white chondrite showing on one face well-marked radiating lines of flow of the fused crust.

DR. G. T. PRIOR: *The Sinai Meteorite.*

The meteoric stone of 1,455 grams which was seen to fall near Kantarah, in the north of the Sinai Peninsula, in July, 1916, is an intermediate hypersthene-chondrite, having a percentage of nickeliferous iron of about 8.6, in which the nickel amounts to about 15 per cent.

G. GREENWOOD: *Communications from the Crystallographic Laboratory of the University of Manchester. No. 1: The Detection of Rotatory Polarisation in an Orthorhombic Crystal exhibiting Crossed Axial Dispersion.*

A plate perpendicular to the acute bisectrix of a crystal of tri-phenyl-bismuthine dichloride, when in the extinction position, transmits a brilliant green monochromatic light due to circular polarisation.

A. F. HALLIMOND: *The Chemical Classification of the Mica Group I.—The Acid Micas.*

## THE COLOUR USERS' ASSOCIATION.

The Annual Meeting of The Colour Users' Association was held at The Milton Hall, Deansgate, Manchester, on June 19, Mr. H. Sutcliffe Smith presiding.

Throughout the year many conferences had been held between the users' representatives of this Committee and the Council, at which difficulties and grievances had been discussed with beneficial effect. Applications on the ground of superiority of foreign quality were now dealt with expeditiously. The chief difficulty was with regard to applications because of price differences. The Licensing Committee officially informed the Association on September 30 last that, as a temporary measure, applications would be granted where the British prices were more than three times pre-war level and where higher than the current foreign prices. When an application was made for a licence the user had to state the price at which he could buy the foreign colour. If the colour could be made in this country, the British makers were given the opportunity of taking the business at the foreign price quoted, or at three times pre-war price, whichever was the higher. If the makers could not accept the order on this basis, then a licence was granted to the users to import. It was understood, however, that the makers' representatives on the Licensing Committee only agreed to meet this foreign price competition provided financial assistance was furnished to the dye manufacturers by the Government. The makers definitely state they cannot at present bring their prices down to three times pre-war level without financial assistance.

### PRICES OF DYEWARES.

The import prices of dyes and dyestuffs, as recorded in the Board of Trade Returns, are at a very high level. For finished Coal Tar dyestuffs (exclusive of Indigo and Alizarine), the following are the averaged prices per pound: 1913, 11s. 7d.; 1920, 79s. 2d.; 1921, 66s. 7d.; and 1922, 65s. 9d. Many conferences have been held throughout the year with the makers and with the Board of Trade on this subject. The users' request to reduce prices to 200 per cent. above pre-war was not an unreasonable one, but the makers had stated that without financial assistance they could not possibly get down to a basis selling price of a maximum of three times pre-war. The

whole cost of establishing the dye-making industry in this country was now being borne by the users. There was a further serious aspect of this situation which required to be considered, and that was the effect of the high prices of British products upon the prices of foreign colour sold in this country. The British makers were not the sole beneficiaries of these high prices, for the foreign producer undoubtedly took full advantage of the artificial condition of the British market consequent upon the Prohibition Act.

#### REPARATION DYESTUFFS.

A deputation from the Council had had an opportunity of visiting the official in charge of the dyestuffs section of the Reparation Commission in Paris. Germany furnished a list monthly of 25 per cent. of its output, which was available for the Allies, who were, within a stipulated period, required to indicate the quantities of colours they desired according to agreed proportions. This country's share was about 4 per cent. of the 25 per cent. It was found, in practice, however, that the U.K. proportion of 25 per cent. of Germany's output of a great many special types of dyes was short of this country's actual needs; on the other hand, there were large quantities of dyestuffs available which were of no interest to us. After several conferences, it was arranged that the German makers should supply more than 25 per cent. of specific dyes on Reparation Account, provided that quantities were not taken in excess of the home consumption, that the export prices were credited to Germany for all quantities above 25 per cent. of each specific dyeware, and that the total quantities were not in excess of 25 per cent. of Germany's total production stipulated under the Committee. At the beginning of each quarter, the Allies were called upon to lodge with the German makers particulars of their requirements under this new arrangement, whereby the German makers would make certain specific colours, which were charged on the following basis:

50 per cent. at the world's lowest price (generally the internal German price).

50 per cent. at the lowest price the I.G. shall have sold at in the receiving country during the month preceding the month of delivery, or during the month of delivery, whichever is the lower.

The users consider this new arrangement of considerable advantage to them, in

that it is a satisfactory means of obtaining through reparation, colour either not made here or not made in adequate quantities.

Unfortunately, however, the price ruling in this country which regulates 50 per cent. of the quantities so imported is an arbitrary one, since, if the bulk of the colour is taken under Reparation, there is no competitive market; the result is that the I.G. can charge such a figure for 50 per cent. of the colour as the resultant average with the remainder at the internal German price gives them a substantial overall selling price. The Association was in close contact with the officials in charge of Reparation dyestuffs in Paris, and it was hoped to bring before them more adequately the users' needs and requirements at regular intervals, and in such a form as would be of practical assistance to them in the taking over of Reparation colour. According to the information furnished by the Board of Trade, it was obvious that this country was not making the fullest use of the facilities afforded by the Reparation Committee, and he would suggest that the whole procedure of obtaining Reparation dyestuffs should now be reviewed in the light of the experience of the past two years.

#### PRICING OF REPARATION DYESTUFFS.

Upon several occasions it had been stated in the House of Commons that prices had been revised from time to time by representatives of the Colour Users' Association. This was not quite in accordance with the actual facts. The Association had protested on many occasions against the high prices of Reparation dyestuffs, and they had had considerable correspondence with the Board of Trade upon the subject.

#### BRITISH DYEMAKERS.

At the last annual meeting he submitted three distinct suggestions bearing on the establishment of the dye making industry with particular reference to the British Dyestuffs Corporation, Limited, namely:— (1) That the Government should wipe out their loan to the Company; (2) that the Company should face a scheme of reconstruction; (3) that the Directors should eventually see their way to arrange that the Corporation shall be managed by men who have been brought up in the industry, on the lines of the big textile associations.

Much progress had undoubtedly been made by this Corporation in the variety and types of the colours which they now

made, and in the improvement in their quality, but there was considerable dissatisfaction among the users on the question of high prices. He wanted to make it perfectly clear that the users did not ask the makers to bring their prices down to the general economic price level, but the makers stated they could not effect any further reductions without serious losses.

#### FOURTH INTERNATIONAL CONFERENCE ON PURE AND APPLIED CHEMISTRY.

The Fourth International Conference on Pure and Applied Chemistry was held from June 18 to 20 at Cambridge. Various reports were presented, and four scientific communications were received and discussed.

Among the matters considered were the reforms in the nomenclature of inorganic and organic chemistry, and the compilation of tables of constants.

Certain matters of importance in industrial chemistry, such as the preservation of foodstuffs, and standardisation in various chemical industries were discussed.

PROF. J. W. MCBAIN, F.R.S., read a paper on *The Study of Soap Solutions and its bearing upon Colloid Chemistry*.

The author pointed out that the study of soaps has so many ramifications, and the phenomena met with are so manifold, that it is only by the exercise of the severest restriction that a clear, general picture can be obtained. Soaps, nevertheless, lend themselves particularly to a study of the colloidal condition and its relation to other states. He dealt with the properties of fluid solutions and clear transparent jellies in the state of complete true reversible equilibrium.

Dilute soap solutions are ordinary crystalloids, whereas more concentrated ones are colloidal electrolytes. Excess of soap above a saturation value separates out in the form of true crystals. The transparent jellies are confined to a portion of the region in which the soap is a colloidal electrolyte. Many soap solutions afford examples of anisotropic liquids.

DR. E. K. RIDEAL read a paper on *Recent Developments in Contact Catalysis*. It is now generally admitted that contact cata-

lysis proceeds through actual contact of the reactants with the catalytic material, although the actual mechanism by which reaction is caused may be brought about by means other than molecular collision, such as radiation or electron transfer. The author discussed diffusion as a factor in catalytic change, the influence of poisons on catalysts, the nature of adsorption compounds, promoter action, etc.

PROF. J. F. THORPE read a paper by himself and DR. C. K. INGOLD on *Some New Aspects of Tautomerism*, in which he defined the term tautomerism and dealt with 1 tautomerism involving the movement of a hydrogen atom and 2 tautomerism which does not involve this movement. The report was based upon the authors' own contributions on the subject.

Prof. F. G. Hopkins gave a report on the Mechanism of Oxidation in the Living Body. He reviewed the previous work on this subject, and drew attention to the problems encountered.

These reports were discussed at sittings of the conference.

#### CORRESPONDENCE.

##### ANALYSIS OF ANCIENT BRONZE.

To the Editor of THE CHEMICAL NEWS.

SIR,—Analysis of several bronze relics dating to the Phœnician and Assyrian periods refute the belief that the bronzes of this time, in some cases, were artificial. The unequal distribution of the constituents coupled with the presence of extraordinary impurities show considerable indications of unaltered constitution through castings.

A comparison between an alloy-ore mined (according to ancient records) at Tel-el-Sifr in South Chaldea (ca. 1500 B.C.) bears considerable similarity to that mined recently in the same locality, showing a general average content of 99.5 per cent. Cu., 0.2 per cent. P., 0.04 per cent. Sn., and traces of As, Bi, Fe, Co, Ni, S and N. That produced from Cyprus (ca. 3500 B.C.) contains less copper and more tin. The proportions, however, are such as to suggest the original natural forms.

These observations may be supported by the following three Biblical references:—

(1) Gen. VI., 22: "And Zillah, she also bare Tubal-cain, an instructor of every artificer in brass and iron." (3870 B.C.).

(2) Deut., VIII., 9: "A land whose stones are iron, and out of whose hills thou mayest dig brass." (2600 B.C.).

(3) Job., XXVIII., 2: "Iron is taken out of the earth, and brass is molten out of the stone." (856 B.C.).

Yours faithfully,  
F. E. LIECHTI.

Church Crookham, Hampshire.  
June 16, 1923.

### NOTICES OF BOOKS.

*Qualitative Organic Analysis—An Elementary Course in the Identification of Organic Compounds*, by OLIVER KAMM. Pp. VII. + 260. London: Messrs. Chapman & Hall, Ltd., 11, Henrietta Street, Covent Garden, W.C.2. 1923. 12s. 6d. net.

The multiplicity of elementary practical manuals on Organic Chemistry is such that a new volume on this subject needs to exhibit some outstanding feature in order to justify its existence.

In the preface of this new American publication on the subject the author states that in 1905 practical organic chemistry was taught in only two or three universities, but in 1918 it was prescribed for all colleges undertaking the training of chemists under the supervision of the U.S. Government.

The course outlined in Prof. Kamm's work follows that which he adopted himself at the University of Illinois, and has for its basis the analytical methods of Prof. Mulliken. It is arranged to cover 32 laboratory periods of 3 hours, and includes the usual experimental work done by students in colleges and technical institutes in qualitative organic derivatives and quantitative analysis. There are also short chapters on the preparation of characteristic exercises.

The book should form a useful guide to lecturers and demonstrators, and will doubtless be adopted by some as a class textbook.

*Klinisches Kolloidchemie*, von DR. ERNEST JOEL. Pp. 124. Dresden and Leipzig: Verlag von Theodor Steinkopff. 1923. Price 2s. 2d.

Dr. Joel's volume on the clinical applications of colloid chemistry is based upon a

course of nine lectures delivered by him on this subject. The lectures and the book are both primarily intended for advanced students and specialists. It is interesting to note how wide are the applications of such an apparently academic subject as colloid chemistry. The author has applied the physico-chemical theories of colloid gel formation and of swelling to the problems of the medical practitioner, for whom much of the book will probably be new.

Prof. K. Spiro, of Basle, has contributed a foreword drawing attention to the coming importance of a knowledge of the applications of colloid chemistry.

The Department of Glass Technology of Sheffield University has published Volume V. of the *Experimental Researches and Reports* which have been collected from the *Journal of Glass Technology*, in which publication they have appeared during the year.

These Reports are collected from the work of Prof. Turner and his collaborators, and include papers on the action of various analytical reagents on glassware, the action of water and steam under pressure on some soda-lime-silicate glasses; and some contributions to the science of glassmaking, and a few articles of a more general type.

The paper on the present position of the glass industry in Czecho-Slovakia is a very discerning one, but it is regrettable that the Czech currency is persistently called kroner instead of kronen. This is perhaps a small point, since the volume contains much that is of considerable value and interest.

### BOOKS RECEIVED.

*The Synthetic Dyestuffs and the Intermediate Products from which they are derived*, by JOHN CANNELL CAIN, D.Sc., and JOCELYN FIELD THORPE, C.B.E., D.Sc. Pp. XV. + 423. Sixth Edition. 1923. Messrs. Charles Griffin & Co., Ltd., Exeter Street, Strand, W.C.2. 21s. net.

*Über Naturprodukte*, by MAX HONIG. Pp. X. + 181. 1923. Verlag von Theodor Steinkopff, Dresden und Leipzig. Price 4s. 4d.

*Atomic Structure and Spectral Lines*, by ARNOLD SOMMERFELD, translated by HENRY

L. BROSE, M.A. Pp. XIII; + 626. Third Edition. 1923. Messrs. Methuen & Co., 36, Essex Street, W.C.2. 32s. net.

The Mellon Institute of Industrial Research of the University of Pittsburgh has just issued its fenth annual report, explaining its objects and achievements.

The Ministry of Agriculture & Fisheries has issued a leaflet, No. 114, entitled, *The Scientific Principles of Feeding Poultry*.

#### PUBLICATIONS RECEIVED.

Bulletins published by the U.S. DEPARTMENT OF THE INTERIOR:—

504: *Surface Water Supply of the United States, 1919-1920. Part IV.—St. Lawrence River Basin.* By NATHAN C. GROVER, W. G. HOYT, C. C. COVERT and C. H. PIERCE. Pp. 188.

729: *Oil Shale of the Rocky Mountain Region.* By DEAN E. WINCHESTER. Pp. 204.

734: *Deposits of Manganese Ore in the Batesville District, Arkansas.* By HUGH D. MISER. With a chapter on the mining and preparation of the ores, by W. R. CRANE. Pp. 271.

735 i.: *Diamond-bearing Peridotite in Pike County, Arkansas.* By HUGH D. MISER and CLARENCE S. ROSS. Pp. 279-322.

735 j.: *The los Burros District, Monterey County, California.* By JAMES M. HILL. Pp. 323-329.

751 A.: *Continuity of some Oil-bearing Sands of Colorado and Wyoming.* By WILLIS T. LEE. Pp. 22.

1.29: *Summary of Mineral Production in Foreign Countries, 1919 and 1920.* By L. M. JONES. Pp. 513-564.

I. 30: *Iron Ore, Pig Iron and Steel in 1921.* By ERNEST F. BURCHARD and HERBERT W. DAVIS. Pp. 565-597.

II. 1: *Fuel Briquets in 1922.* By W. F. MCKENNEY. Part II. Pp. 4.

*Revision of the Flora of the Green River Formation with Descriptions of New Species.* By F. H. KNOWLTON. Pp. 133-182.

*Fossil Plants from the Tertiary Lake Beds of South-Central Colorado.* By F. H. KNOWLTON. Pp. 183-197.

*The Fauna of the So-called Dakota formation of Northern Central Colorado and*

*its Equivalent in South-Eastern Wyoming.* By JOHN B. REESIDE, JUN. Pp. 199-207.

#### PUBLICATIONS RECEIVED FROM THE U.S. DEPARTMENT OF THE INTERIOR, BUREAU OF MINES.

*The Universal and the Fireman's Gas Masks,* by S. H. KATZ, J. J. BLOOMFIELD, and A. C. FIELDNER. Pp. 22.

*Metal-Mine Accidents in the United States during the Calendar Year 1921,* by WILLIAM W. ADAMS. Pp. 96.

*The Chloride Volatilisation Process of Ore Treatment,* by THOMAS VARLEY, E. P. BARRETT, C. C. STEVENSON, and ROBERT H. BRADFORD. Pp. 99.

*Bibliography of Petroleum and Allied Substances in 1919 and 1920,* by E. H. BURROUGHS. Pp. 374.

*Preparation, Transportation, and Combustion of Powdered Coal,* by JOHN BLIZARD. Pp. 127.

The Dominion Bureau of Statistics, Canada, has just published a report entitled *Chemicals and Allied Products in Canada, 1921*. It contains a summary of the statistics on the production of chemicals in Canada during the year.

From a perusal of these statistics in the various chemical industries, it is noticed that production in almost every industrial field during the past three years shows the effect of post-war influences. In 1919, as a result of the large scale production during the war years, the accumulation of stocks was considerably in excess of current requirements, with the result that production was much curtailed. Most of these stocks were disposed of in 1919 with the result that in the early part of 1920 an appreciable advance in prices occurred which reached a maximum about the middle of the year. This advance was followed by increased production in many industries. During the closing months, however, demands from consumers for lower prices became more insistent, and in 1921 a deflation in prices occurred. At the close of that year, although prices were at a much lower level than at the beginning, conditions through-

out the industry were much improved, and prospects were much better.

An illustrated catalogue of Astronomical Photographs, including lantern slides, transparencies, and prints from negatives made at the Yerkes Observatory, has just been issued. It is the third edition of this catalogue issued by the University of Chicago Press.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Latest Patent Applications.*

- 13835—Cosway, H. C.—Manufacture of methyl chloride and ethyl chloride. May 25.
- 13752—Metals Production, Ltd.—Leaching copper. & Co. May 24.
- 13502—Oderberger Chemische Werke Akt-Ges.—Production of colloidal solutions and resolvable dried residues from irreversible colloids. May 22.
- 14501—Chemische Fabrik Griesheim-Elektrom.—Manufacture of azo-dyestuffs. June 1.
- 14268—Brutkzus, M.—Process for effecting chemical reactions. May 30.
- 14079—Chemische Fabrik auf Action vorm E. Schering.—Manufacture of barbituric-acid compounds. May 28.
- 14293—Grasselli Chemical Co.—Manufacture of concentrated acetic acid. May 30.
- 14013—Green, H.—Reduction of oxides and oxy-compounds. May 28.
- 14325—Jaques, A.—Manufacture of barium sulphate. May 31.
- 14672—Chemische Fabrik Griesheim-Elektrom.—Manufacture of acylacetyl compounds. June 4.
- 14945—Soc. of Chemical Industry in Basle.—Manufacture of naphthioindoxyls. June 7.

*Specifications Published this Week.*

- 183419—National Aniline & Chemical Co., Inc.—Production of vat dyes.
- 197573—Marks, E. C. R.—Zirconium alloys and and Hirschberg, Z. von.—Manufacture of processes of making same.

- 182781—Deutsch-Englische Quarzschmelze Ges., quartz and the like articles non-pervious to gases.
- 197706—Meter, J. W. van.—Method of producing poisonous gases.
- 197724—Pease & Partners, Ltd., and Stephenson, G.—Manufacture of sulphate of ammonia.
- 197845—Prentice, A. T.—Method of and apparatus for burning sulphate.
- 197898—Rhenania Verein Chemischer Fabriken Akt-Ges.-Zweigniederlassung Mannheim and Rusberg, Dr. F.—Manufacture of alkali thiosulphate.

*Abstract Published this Week.*

- 196023—Methane.—Hilditch, T. P., Birchdene, Cross Lane, Grappenhall, Cheshire, and Crossfield & Sons, Ltd., J., Warrington, Lancashire.

Methane is produced by passing commercial water gas, containing approximately equal proportions of carbon monoxide and hydrogen, over a catalyst maintained at a temperature of 220-300° C. and preferably not higher than 280° C. The reaction takes place according to the equation:— $2\text{CO} + 2\text{H}_2 = \text{CO}_2 + \text{CH}_4$ . The catalyst is nickel or cobalt or a mixture thereof, and is preferably mounted on a carrier. The process may be applied to the methanation of water gas or to the production of pure methane. In the latter case, carbon dioxide is first eliminated and then residual traces of carbon monoxide and hydrogen are removed by passage over heated copper oxide at a temperature of 200-250° C., the methane being finally separated from nitrogen by liquefaction.

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EDITED BY

*JAMES H. GARDINER, F.Inst.P., F.C.S.*

*and*

*J. G. F. DRUCE, M.Sc. (Lond.), R.Nat.Dr. (Prague).*

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No. 3299.—JULY 6, 1923.

## THE CHEMICAL NEWS,

VOL. CXXVII. No. 3299.

### GLASS MAKING IN ENGLAND.

The great war and the industrial struggle that is following it has profoundly influenced many British industries, but upon none has the effect been so pronounced as upon that of glassmaking.

Glass is so familiar to all of us that we often fail to realise the magnitude of the industry. There is probably not a man, woman, or child but handles glass in some form or another many times in each day of their life, and when one considers the fragility of the ware, it is apparent that the labour involved in its preparation and fabrication must be enormous.

Apart from the domestic use of glassware there is scarcely an industry in existence that does not need glass in some form or other, and for the progress of chemistry and physics the production of good glassware is a matter of vital importance.

The war brought home to all of us the need for what has been called scientific glassware, as without it research in any direction is practically impossible. The immediate result was the formation of the Glass Research Association, the Society of Glass Technology, and other bodies. Many manufacturers extended their works, new factories have come into existence, and there is every indication that great progress has already been made in the industry. Great strides have been made in America

in mechanical appliances for the production of glassware, and machines have been erected in England for the rapid manufacture of bottles, jars, and other domestic necessities, and containers in glass are now being produced in England daily by the million.

Glassmaking as a fine art has been practised in England for a great many years, and the recent publication of a beautifully illustrated work on the art of glassmaking, by the late Harry J. Powell,\* who, until lately, managed the old Whitefriars Glass Works in the City, brings the beauty of the craft into full prominence. Mr. Powell was probably the most successful producer of truly art glassware in England, and he devoted his whole life to the work, his book will for many years rank as one of the art treasures of the country. Mr. Powell was very much concerned lest the art of glass-craft should die out in England, and there undoubtedly are indications that the labour conditions of recent years are such that the production of successful craftsmen is not promising, but for all that there are those who do not regard the problem as hopeless, and we understand that in the new Whitefriars glassworks that have been erected at Wealdstone, Middlesex, serious efforts are already being made for the systematic training of glassworkers to take the place of the old-world craftsmen who produced the exquisite examples illustrated in the work in question. The members of the Society of Glass Technology, in company with Professor Turner, of Sheffield University, recently visited the newly launched glassworks, and the party were shown the modern furnaces, annealing ovens, kilns and elaborate work-

shops erected by the company, and there appears to be genuine hope that the disaster feared by Mr. Harry Powell will be averted by meeting modern labour conditions by modern methods of treatment. The educational advantages possessed by the youth of the present day should largely compensate for the fact that he is not allowed to take up work that involves the night duties of a glassblower until he has passed the age of sixteen, whereas some of the craftsmen mentioned in Mr. Harry Powell's book commenced work when eight or nine years of age. The fact that many of these men, although now with records of more than 40 years' service, are still hale and hearty, shows that the work is not unhealthy.

Those who read Mr. Harry Powell's book will not fail to be impressed with the beauty of the manufacture, and will endorse our opinion that every effort should be made to ensure the continuance of one of the most charming of British industries.

J.H.G.

\* "Glass-making in England," by H. J. Powell, C.B.E., Cambridge, at the University Press, 1923.

## STUDIES ON CATALYTIC ACTION.

### II.—CATALYTIC PREPARATION OF PARA-CYMENE AND ITS FORMATION IN SULPHITE TERPENTINE.

By SHIGERU KOMATSU, HISASHI NAKAMURA, AND MASAO KURATA.

Klason<sup>1</sup> first noticed that the etherial oil collected during the manufacture of pulp from spruce by the sulphite process, consists mainly of para-cymene and not of terpenes. Sulphite terpentine from the pulp mills of U.S.A. was studied by Herty and Graham,<sup>2</sup> A. W. Schorger<sup>3</sup> and M. Philips<sup>4</sup> with a view to the utilisation of para-cymene in it. O. Asehan<sup>5</sup> and J. Alfthan<sup>6</sup> have, also, studied the terpentine in Finland.

The sulphite terpentine, we studied, was obtained from the pulp mill at Ochiai, Karafuto, where sulphite pulp was manufactured from Yezo-matsu and Todo-matsu. The crude oil which amounted to 140 gm., was dark brown in colour,  $d_4^{15} = 0.965$ . It was subjected to steam distillation and a light-yellow oil was obtained, which, after drying with anhydrous sodium sulphate, was distilled:

First fraction, B.p., 174-270° 70 gm.  
Second fraction, B.p., above 270° 35 gm.

Two fractions were fractionated on metallic sodium, and the fraction boiling at 173-175° was collected. The yield was 50 per cent. of the crude oil.

The physical constants and the elementary composition of the purified substance were determined with the following results:

It gave C=89.33; H=10.34; ( $C_{10}H_{14}$ , requires C=89.48; H=10.52),  $d_4^{25} = 0.85381$ ;  $n_D^{25} = 1.4821$ ; M.R.=44.80.

For identification with para-cymene, it was oxidised with potassium permanganate into tere-phthalic acid<sup>7</sup> and para-hydroxyisopropyl benzoic acid<sup>8</sup> and the latter melts at 156° and gave on analysis C=66.23; H=6.64; ( $C_{10}H_{12}O_3$ , requires C=66.64; H=6.72).

On the other hand, the substance was sulphonated with conc. sulphuric acid following Claus' directions,<sup>9</sup> and sodium salts of mono- and di-sulphonic acids were separated by aid of their solubility in alcohol solution, and di-sulphonic acid salt was analysed; Ba = 31.32 ( $C_{10}H_{12}O_6S_2Ba$  require Ba=31.95).

Terpenes of the formula  $C_{10}H_{16}$  by dehydrogenation, were ultimately converted into para-cymene; consequently the transformation was sometimes made use of in the determination of the constitution of the compounds.<sup>10</sup>

Kekule<sup>11</sup> has studied the conversion of terpene into cymene by oxydation with phosphorous sulphide. L. Ruzika, J. Meyer and M. Mingazzini<sup>12</sup> have obtained para-cymene from limonene and terpinene by catalytic oxydation with sulphur, fol-

<sup>1</sup> Ber. D. Chem. Ges., 1900, XXXIII., 2343.

<sup>2</sup> J. Ind. and Eng. Chem., 1914, VI., 803.

<sup>3</sup> Ibid., 1918, X., 258.

<sup>4</sup> J. Amer. Chem. Soc., 1922, XLIV., 1775.

<sup>5</sup> Zellstoff Chem. Abhand., 1920, 1, 73.

<sup>6</sup> Ber. D. Chem. Ges., 1920, LIII., 78.

<sup>7</sup> R. Fittig, A. Korbrich and T. Jilke: Lieb. Ann., 1868, CXLV., 144.

<sup>8</sup> O. Wallach: Ibid., 1891, CCXIV., 10.

<sup>9</sup> Ber. D. Chem. Ges., 1881, XIV., 2140.

<sup>10</sup> V. Meyer and P. Jacobson: Lehrbuch d. Org. Chem., 1902, II., 110.

<sup>11</sup> Ber. D. Chem. Ges., 1869, II., 121.

<sup>12</sup> Hel. Chim. Acta., 1922, V., 356.

lowing Vesterberg's directions,<sup>13</sup> and the same process was applied by W. Friedmann<sup>14</sup> to naphthene hydrocarbons.

The authors have succeeded in the catalytic preparation of para-cymene, the main constituent of sulphite terpine, from pinene and menthene respectively.

136 gm. pinene obtained from commercial terpine oil, were heated with 70 gm. sulphur in a flask at 200° for 23 hours, the reaction product was distilled under reduced pressure and 71.5 gm. of the product was obtained. It was distilled under ordinary pressure after treating with 10 per cent. caustic soda solution, dried with calcium chloride, and a fraction boiling at 170-275° was collected. The yield was 55 gm. (52 per cent. of the theoretical).

The product, thus obtained, on distilling with metallic sodium, was all distilled out between 165-175°. It was purified by repeated distillation with metallic sodium.

The purified substance  $d_4^{25} = 0.8542$ ;  $n_D^{25} = 1.4743$ ; M.R. = 44.41, was analysed: it gave C = 88.37; H = 11.34; (C<sub>10</sub>H<sub>14</sub> requires C = 89.45; H = 10.55).

It was oxydised with potassium permanganate into para-hydroxyisopropyl benzoic acid<sup>15</sup> which melted at 156-156.5° and gave C = 66.44; H = 6.33; (C<sub>6</sub>H<sub>4</sub>C(OH)(CH<sub>3</sub>)<sub>2</sub>-COOH requires C = 66.64; H = 6.72).

In the same manner, menthene prepared from menthol by catalytic dehydration with thoria was transformed into para-cymene.

140 gm. menthol were passed on thoria heated at about 400°, and yield 125 gm. light greenish yellow liquid substance,  $d_4^{25} = 0.817$ , which distilled between 155-210°. It was purified by repeated distillation with metallic sodium, and the following fractions were obtained:

The fraction boils at 145-164° under 752 mm., with 10 per cent. of the yield.

Other fraction boils at 164-167° under 752 mm., with 40 per cent. of the yield.

The second fraction was confirmed by analysis to consist of menthene,<sup>16</sup>  $d_4^{25} = 0.8096$ ;  $n_D^{25} = 1.4469$ ; M.R. = 45.60; which gave C = 86.10; H = 12.92; (C<sub>10</sub>H<sub>18</sub> requires C = 86.87; H = 13.13).

Menthene, thus obtained, was heated with sulphur at 200° for 24 hours, and the reaction product was subjected to distillation on metallic sodium to purify. The cymene fraction boiling at 170-173.5°,  $d_4^{25} = 0.8389$ ;  $n_D^{25} = 1.4740$ ; M.R. = 44.94; gave on analysis C = 87.68; H = 10.92, (C<sub>10</sub>H<sub>14</sub> requires C = 89.45; H = 10.55).

The conversion of menthol and borneol by simply heating with sulphur at about 200° into cymene, was tried, but with no result.

Terpenes of the formula C<sub>10</sub>H<sub>16</sub>, on the contrary, can easily be transformed into cymene by catalytic oxydation with sulphur.

Aromatic hydrocarbons and their oxygen derivatives, such as para-cymene and safrol are widely distributed, being generally associated with the essential oils in plants. The origin and the mechanism of the formation of the aromatic compounds in the flora were interesting problems.

As to the formation of para-cymene in sulphite terpine, Klason<sup>17</sup> has already put forward the following opinion:

"Alles Terpentinöl soll ja auch nach den vorhandenen Angaben etwas Cymol enthalten, und im Holze sind die aetherische Oele lange Zeit dem Einfluss der Luft ausgesetzt worden. Wie man nun diesen Uebergang im Lichte der Engler'schen Theorie der Autoxydation erklären soll, mögen künftige Untersuchungen darthun. Entweder wurden von der zunächst entstandenen superoxydartigen Verbindung zwei Wasserstoffatome direct wegoxydirt oder es entsteht intermediär ein Alcohol, welcher durch Wasserabspaltung in Cymol übergeführt wird." Much more probably the formation of cymene in wood may be attributed to the autoxydation of etherial oils, as Klason stated. Whether the sulphite terpine was formed in a digester during the manufacture of pulp, by the same mechanism is very doubtful.

Our hypothesis, however, for the formation of the sulphite terpine, is quite different from Klason's, and is grounded on the experiments described above; the terpene existing in the wood would probably be transformed during the manufacture of pulp by the sulphite process, into para-cymene by catalytic oxydation with sulphur which is liberated in a free state in the digester.

<sup>17</sup> *Loc. cit.*

<sup>13</sup> *Ber. D. Chem. Ges.*, 1903, XXXVI., 4200.

<sup>14</sup> *J. Chem. Soc.*, 1917, CXII., 13.

<sup>15</sup> *O. Wallach: Loc. cit.*

<sup>16</sup> *P. Walter: C.R.*, 1838, VI., 473; *Lieb. Ann.*, 1839, XXXII., 288.

The evidences in favour of our view of the formation of sulphite terpenine, are easy to quote here from literature.

Shinozaki<sup>18</sup> has isolated from the essential oils obtained by steam distillation of Yezo-matsu and Todo-matsu pinene and phellandrene, which were proved by our experiments to transform into para-cymene.

We cannot pass over without mentioning here the most important fact that free sulphur actually exists in the acid-liquor used for pulp manufacture, cited in Klason's article.<sup>19</sup>

—(From the *Memoirs of the College of Science, Kyoto Imperial University*, Vol. IV., Mar., 1923.)

THE REPORT OF THE CHEMICAL  
EXAMINER'S DEPARTMENT (PUBLIC  
HEALTH), GOVERNMENT OF  
MADRAS.

Read—the following papers:—

Letter from Major Clive Newcomb, M.D., A.I.C., I.M.S., Chemical Examiner to Government, to the Secretary to Government, Local Self-Government Department (through the Surgeon-General with the Government of Madras, Madras), dated Madras, the 26th March, 1923, No. 538.

The following is abstracted from the Report for 1922:—

MEDICO LEGAL INVESTIGATIONS.

In the 220 cases of suspected human poisoning investigated, poison was detected in 108, giving a percentage of detections of 49.1 as compared with 40.6 in the previous year.

It is a matter for regret, as previous Chemical Examiners here have remarked, that more time is not available for trying new toxicological methods. In all branches of practical chemistry, but especially in toxicology, new tests or methods of analysis, even if most carefully described, cannot be put into practice without many controls and personal investigations by the analyst. A little, however, has been done.

In the extraction of morphine from viscera, a method which had been used here

before was again tried on some cases, in view of its recommendation in Lucas' *Forensic Chemistry*. Of the evaporated acid alcoholic extract of the viscera, a small portion was extracted with ether in the presence of sodium bicarbonate for the porphyroxin test. To the remainder sodium hydroxide was added, and it was then extracted first with ether, next with chloroform to remove other alkaloids, and thirdly with a mixture of ethyl acetate and ether to extract the morphine. In a case in which both dhatura and opium were suspected and in which this procedure was used, the presence of a mydriatic alkaloid was proved in the chloroform extract and the presence of morphine in the ethyl acetate-ether extract, in addition to positive porphyroxin and meconic acid tests. In another case an infant aged two years was suspected to have died from an overdose of opium, but in this case the porphyroxin test was the only one which was positive. The porphyroxin test is said to be a very delicate and reliable one for Indian opium.

Beam's test for Cannabis Indica, both in its original and modified form (*vide* Lucas' *Forensic Chemistry*) was tried on a sample of charas from the Punjab and found to work well.

Some experiments were made by Dr. S. Rajagopal Nayudu, to try to find tests for madar. An alcoholic extract of any part of the plant except the juice after evaporation to dryness and taking up in water gave crystals with a saturated solution of iodine in 10 per cent. potassium iodide, which bore some resemblance to Florence's crystals, and crystals with saturated aqueous picric acid of probably a characteristic shape. The alcoholic extract of the juice on evaporation left an orange yellow, bitter, poisonous resin, which gave a bluish colour with strong hydrochloric acid and green colour with strong sulphuric acid. White dilute acids, it gave a fine pink colouration. Beam's test was negative with madar juice. In two cases of suspected madar poisoning we were able to extract a bitterish resin from viscera which proved fatal to a frog and gave the above reactions. The cases, therefore, presumably were of madar poisoning, but this could not be considered to be conclusively proved.

The test for arsenic described in the *J.C.S.Abs.*, 1922, page 584, was tried, and found to work well with a solution of arsenious acid. The quinine molybdate test

<sup>18</sup> *Kogyo-Kwagaku Zasshi*, 1912, XV., 730.

<sup>19</sup> *Uregelmassige Gang v. Sulphitstoff-Kochung u. deren Ursache*, 1910, p. 63.

described in the *Analyst*, 1922, page 317, was tried and found to work satisfactorily.

Some experiments were made on the adsorption of brucine sulphate from dilute aqueous solution by kieselguhr with a view to the possibility of using adsorption for the extraction of alkaloids from viscera.

In these experiments the brucine was estimated by evaporating to dryness and weighing the residue of a measured quantity of the solution before and after adsorption, making a small allowance for the amount of soluble substances dissolved from the kieselguhr.

The estimation of brucine in dilute solution by precipitation with Dragendorff's reagent (Bismuth potassium iodide) was also tried. The amount of precipitate was estimated by means of a simple form of nephelometer. This was simply a glass rod graduated into millimetres along its stem with a short platinum wire bent at right angles to the rod at one end. It was pushed into the suspension of the precipitate holding the stem vertical till the platinum wire could no longer be seen and the length of rod immersed noted. The method was quick but only accurate to within about 10 per cent.

#### GENERAL ANALYSES.

The number of these analyses done during the year was 570, against 564 in 1921.

The Customs department sent 144, of which 50 were analyses of gold or silver thread or lametta. These frequently gave small traces of gold or silver, probably indicating they were plated with the real metals.

The General Hospital, Madras, sent 122 articles for analyses, of which 106 were stomach washes after test meals. Our routine in examining these is to estimate free hydrochloric acid by Buntzberg's method, total acidity by titration with  $N/10$  soda, using phenolphthalein as indicator, and to test qualitatively for lactic acid by Uffelmann's method. A direct estimation of the hydrogen ion concentration would probably be of more value, and with this end in view solutions of standard  $P_h$  are being prepared. Whenever possible, these are prepared by two methods and the colours given by various indicators compared. A great deal of care is needed in the preparation of the standard solutions and in purifying the chemicals used to get perfect matches.

The danger of relying on the labels of bottles for more than an approximate indication of their contents was well illustrated

by the case of a bottle labelled "Pure saccharose," which was being used in the Hygiene Laboratory as a standard in work with a polarimeter. It was sent to us because of the discordant results which were obtained, and on analysis was found to contain a very considerable amount of glucose.

The accurate determination of the density is often a most useful test of purity of a liquid or a check on the determined strength of a solution. To take a specific gravity with a bottle takes a considerable time even at the temperature of the laboratory, and at any other temperature requires a carefully regulated thermostat. Most densities are given at (15° C.), and in Madras to keep a thermostat at a temperature lower than about 30° C. would require prohibitive quantities of ice. An investigation was therefore made into the accuracy obtainable with an ordinary Westphal's balance and some previous calibrations of one of our balances carefully revised. The reading of the balance can be made very quickly and with a liquid which is changing in temperature fairly rapidly a series of readings can be taken, the mean of which should be reliable to within + 0.0003. Some experiments have been made during the year, as time could be found for them, to see if a more useful test for the purity of chloroform could not be devised using this instrument, than the present B.P. test of taking the specific gravity at 15° C. B.P. chloroform contains a small quantity of alcohol as a preservative. It was considered that if this alcohol were removed and the density determined before and after removal this might afford a measure of both the amount of added alcohol and the purity of the residual chloroform. The alcohol can be easily extracted from chloroform by washing it with water. Five washings with a bulk of water equal to that of the chloroform each time are sufficient. The density of the chloroform may be determined wet and a small allowance made for the wetness. Experiments to determine the changes in density produced by water, alcohol and temperature are still going on.

We were consulted about a "disease" developed by some mercury used in a light-house to float the revolving part of the lamp so as to make it turn easily. A sample of the diseased mercury showed that it had become partly converted into a grey viscid, slimy substance. On examination it turned out to be an emulsion of mercury and oil,

of such a consistency as to effectually clog almost any mechanism.

On another occasion we were asked to match a special lubricating oil for an electric machine used at the Ophthalmic Hospital, Madras. We obtained two lubricating oils, one slightly more viscid and one rather less viscid than the sample, and by testing the viscosity of mixtures of the two found the proportion in which they had to be mixed to match the sample as regards viscosity. The difficulty in this case was that only about 2 cc.'s of the sample were available, so that the ordinary types of viscosimeter (except Ostwald's which we did not then possess) were inapplicable. The viscosities were measured by noting the times taken for 0.5 cc. of the oil to run out of a 1 cc. pipette graduated into 1/100ths. We could not match both the viscosity and the density, so we recommended a mixture which made the viscosity right, and I understand that machine has been running well on our mixture since.

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#### PROCEEDINGS AND NOTICES OF SOCIETIES.

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##### THE ROYAL SOCIETY.

THURSDAY, JUNE 28.

Papers read:—

V. H. BLACKMAN, F.R.S., A. T. LEGG, and F. A. GREGORY. *The Effect of a Direct Electric Current of very Low Intensity on the Rate of Growth of the Coleoptile of Barley.*

The coleoptile (sheathed plumule or young stem) of barley seedlings are exposed to an electric discharge from a point charged *positively* to about 10,000 volts (crest value) and placed at such a height above the coleoptile that a current of  $0.5 \times 10^{-10}$  amp. passes through it, the current density being  $4 \times 10^{-9}$  amp. per cm.<sup>2</sup> Under these conditions the rate of growth is markedly accelerated from the first hour onward, showing in the third hour a percentage increase above that of the control plants of 7.53 + 1.95.

After the cessation of the current a well-marked "after-effect," greater than the direct effect, is to be observed, the enhanced rate of growth steadily continuing and showing a percentage increase of 15.68

+ 2.62 above that of the controls. The after-effect is greater with a short period of discharge of one hour than with a longer period of three hours.

When the point is *negatively* charged the rate of growth is increased during the first hour, but the increase, instead of becoming greater with time, as with a current in the other direction, becomes less. An after-effect follows here also, but it is markedly less than that resulting from a positive discharge.

Experimental evidence is advanced for the view that the gaseous products of the discharge and the "electric wind" play little or no part in the stimulation of growth observed. The current alone appears to be of importance, a view which is supported by the fact that its direction exerts such a marked influence on the degree of stimulation.

M. S. PEMBREY, F.R.S., N. W. MACKEITH, W. R. SPURRELL, E. C. WARNER, and H. J. WESTLAKE. *Observations on the Adjustment of the Human Body to Muscular Work.*

Papers read in title only:—

MISS R. M. TUPPER-CAREY and J. H. PRIESTLEY. *The Composition of the Cell Wall at the Apical Meristem of Stem and Root.* Communicated by Dr. F. F. Blackman, F.R.S.

The walls of the apical meristem of stem and root differ in the ease with which cellulose may be detected in them with iodine reagents. As the result of macro-chemical and micro-chemical experiment it is concluded that the cellulose in the wall of the root meristem is masked by its combination with other substances, particularly proteins and fatty acids. In the shoot meristem the cellulose is closely linked with larger quantities of pectin but less protein and fatty acid are present, especially when the shoot is growing in the light. These conclusions seem to throw further light upon the comparative difficulty with which diffusion appears to take place through the apical meristem of the root compared with that of the shoot.

L. J. HARRIS. *The Titration of Amino and Carboxyl-Groups in Amino-Acids, Polypeptides, etc.* Communicated by Prof. F. G. Hopkins, F.R.S

F. A. E. CREW. *Studies in Intersexuality.—II. Sex-reversal in the Fowl.* Communicated by Prof. R. C. Punnett, F.R.S.

W. FINKLER. *Analytical Studies on the Factors causing the Sexual Display in the Mountain Newt (Triton alpestris).* Communicated by Prof. E. W. MacBride, F.R.S.

G. A. SCHOTT, F.R.S. *On the Scattering of X- and  $\gamma$ -Rays by Rings of Electrons.—The Effect of Damping of the Incident Radiation.*

The object of the investigation is to examine the effect of the damping of incident X- and  $\gamma$ -rays on their scattering by revolving rings of electron, with the view of determining whether the diminution of the total scattering observed by Ishino for aluminium, iron and lead can be attributed wholly or partly to this cause. Damping of the usual type, of an amount compatible with the production of moderately sharp lines in the X-ray spectrum, is found to increase slightly the total scattering of short waves, such as the hard  $\gamma$ -rays used by Ishino, although it decreases slightly that of long waves. A single electron ring, however, such as we postulate in hydrogen and ionised helium on Bohr's theory, is completely unaffected by this type of damping. It is hardly possible that damping can diminish the total scattering for any type of atom below the amount required by the Simple Pulse Theory, certainly not to the extent required by the experiments of Ishino and the more recent ones of A. H. Compton.

P. A. MACMAHON, F.R.S. *On a Class of Transcendents of which the Bessel Functions are a Particular Case.*

L. C. MARTIN. *The Photometric Matching Field.* Communicated by Prof. H. L. Callendar, F.R.S.

During a previous investigation it was noticed that an improvement in the visibility of faint contrasts observed with central vision could be obtained by stimulating the peripheral regions of the retina. Some explanations of this and allied effects are discussed. As a practical application experiments are described which show that an increase in precision of the order of 30 per cent. can be obtained in photometric matches by surrounding the photometric

field with a larger area of approximately equal brightness.

G. P. THOMSON. *Test of a Theory of Radiation.* Communicated by Sir Joseph Thomson, F.R.S.

Experiments are described with positive rays which show that visual and photographic effects can be obtained with trains of waves shorter than those produced in the emission of a quantum of light.

A. LL. HUGHES and P. LOWE. *Intensities in the Helium Spectrum.* Communicated by Prof. H. A. Wilson, F.R.S.

The distribution in intensities in the helium spectrum, when excited by impacts between electrons and atoms, has been studied as a function of the energy of impact of the electrons, all other variables being held constant. The energy of impact varied from 34 volts to 210 volts.

The outstanding result of the work is that the curve showing the intensity of any spectrum line as a function of the energy of impact is characteristic of the series to which it belongs. The intensities in the Doublet System all decrease rapidly as the energy of impact is increased from 34 volts. The rate of decrease is greatest for  $1\pi-m\sigma$  and least for  $1\pi-m\delta$ . The Principal Series,  $1S-mP$ , of the Singlet System is characterised by a very great increase in intensity as the energy of impact is increased from 34 volts up to about 80 volts, beyond which there is little change. The lines of the Diffuse Series,  $1P-mD$ , all show a maximum at about 75 volts, the rise to maximum being progressively greater the higher the term number of the line. The lines of the Sharp Series,  $1P-mS$ , after a small initial rise to 60 volts decrease slightly.

A. A. DEE. *The Effect of Quenching from above the Carbide Transition Temperature upon the Magnetism of Steel.* Communicated by Prof. S. W. J. Smith, F.R.S.

The first accurate determination of a transition point in iron carbide at which the ferromagnetism disappears during heating, in a similar way to that of iron at the critical temperature of the latter, was made by S. W. J. Smith in 1912. It has recently been suggested by Thompson and Whitehead that this carbide transition, described as from  $\alpha$  to  $\beta$  cementite, is such that the carbide can be retained in the  $\beta$  condition by quenching from above the transition

temperature. The experiments described in the present paper show that the magnetism of steel at ordinary temperatures is not materially altered by quenching of the kind above described and, therefore, that the return of the carbide to the ferromagnetic state is not retarded by sudden cooling from above the transition temperature.

T. S. P. STRANGEWAYS and H. E. H. OAKLEY. *The Immediate Changes Observed in Tissue Cells after Exposure to Soft X-Rays while growing "in vitro."* Communicated by W. B. Hardy, Sec. R.S.

Tissue cultures *in vitro* were exposed to soft X-rays for gradually increasing periods, varying from 5 minutes to 2 hours.

Four cultures were exposed at a time: two of these were stained immediately, and two after being returned to the incubator for 80 minutes. It was found:—

(1) That there was a latent period of about 15 to 20 minutes before the changes produced in the cells by irradiation can be recognised.

(2) That after 5 minutes irradiation development of new dividing cells was lessened. After exposure of 20 minutes or longer the formation of new dividing cells practically ceased.

(3) After exposure of 5 minutes granular changes and fragmentation of the chromosomes were observed in some cells in mitosis at metaphase and anaphase. After 15 minutes' irradiation the majority of cells in mitosis showed these changes, and also a definite lag in the passage of some chromosomes to the poles of the spindle, and often a definite lag in cell-division itself, but in spite of these changes in the chromosomes many, if not the majority, of the cells passed through the various phases of mitosis and completed division. After the longer exposures, however, some of the resulting daughter-cells showed abnormality.

(4) After exposure of 25 minutes or longer some cells in mitosis showed clumping of the chromosomes at metaphase.

(5) As time of exposure increased there was increase in size and alteration in structure of cytoplasm, nucleus and nucleolus of some fully formed cells.

(6) After an exposure of 60 minutes or longer, definite changes occurred in cytoplasm, nucleus and nucleolus of some cells. These affected cells became disorganised and showed irregular and vary-

ing outline. Eventually cytoplasm and nucleus broke up, disintegrated and appeared to go into solution in the surrounding medium.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

A general meeting of the members was held on Monday, July 2, 1923.

#### NATIONAL ENGINEERS' ASSOCIATION.

ADDRESS BY W. H. CASMEY, C.E., AT WAKEFIELD, JUNE 25.

Had I the qualifications of an artist instead of being a critic of smoky chimneys, I should paint three historical pictures which would have no equal in the National Gallery, and the subjects would be:—

First picture, entitled *The Birth of Power 687*, and would indicate a tall, monkish figure, with a basket of blackberries on one arm and a lump of coal under the other.

The second picture would show a finely built, solid-looking Yorkshireman, gazing at a smoky chimney, and the title would be *Green's Common Sense, 1845*.

My third artistic effort would show a big pile of coals, on which would appear in white letters, "Thirteen hundred million tons," and above would be a dense mass of black clouds, and this should have the title of *Coals, Clouds, and Wastage, 1923*.

The first picture would represent the Monk of Glastonbury Monastery, who, whilst gathering blackberries in an old quarry in the year 687, came across an outcrop of coal, and, not having seen what he terms "black stone" before, took a piece for the inspection of the prior, and he, after examination, considered it of no consequence, and told his man to throw it on to the fire. Wood was the only fuel then used.

The black stone, helped by the wood fire, soon made the principal of the Monastery interested, and from this time, coal was the only fuel used there, and the secret of its heating power was kept for over 100 years, and was then shared with a monastery in Northumberland, and it is probably due to this that Newcastle coals were so much in demand in the south two or three centuries later.

If we now make a leap forward of 1,000 years, we are in the company of James



Watt and others in Cornwall, and see their efforts in constructing a steam generator, which finally developed into the Cornish boiler.

Another stride of 50 years, and we reach 1800, in which year the first steam mill in Bradford was started, the engine of which developed 15 horse power.

Mr. Ed: Gréen, of Wakefield, recognising the huge wastage of coal from steam boilers, conceived the idea of building up a business by utilising the waste heat for heating the water before passing it into the boiler, and this invention, the Green's Economiser, is now a household word wherever steam boilers are in use, and for many years may be considered as having saved steam users eight to ten million tons of coal per year.

Mr. Brownlie, in his tests of 1,000 boilers, found the average overall efficiency was 60 per cent., the maximum being over 80 per cent., the minimum under 50 per

cent. Now, is there any reason in allowing such conditions? Twenty-two boilers out of 1,000 boilers giving over 80 per cent., and others 30 per cent. lower; in other words, 14s. worth of coal in one case doing the work of 20s. in another.

Let us look at the subject more closely, and we find the average CO<sub>2</sub> readings were 7 per cent.; this indicates 33 lbs. of air per lb. of coal, and if the calorific value of the coal averaged 12,500 B.Th.U.s, the average furnace temperature would be 1,506 degrees.

By decreasing the air supply to 18 lbs. of coal, the CO<sub>2</sub> readings will be 13 per cent. and the furnace temperature 2,797 degrees, a difference of 1,291 degrees by reducing the air supply per lb. of coal from 33 lbs. to 18 lbs. A difference of 1 per cent. CO<sub>2</sub> shows an average difference in furnace temperature of 215 degrees. The actual figures per 1 per cent. CO<sub>2</sub> are as follows:—

With	7 p.c. CO <sub>2</sub>	Gases per lb. of coal	33.8 lbs.	Furnace temperature	1,506 degrees.
"	8 p.c.	" " " " "	29.8	" " " "	1,748 "
"	9 p.c.	" " " " "	25.5	" " " "	1,962 "
"	10 p.c.	" " " " "	24.0	" " " "	2,170 "
"	11 p.c.	" " " " "	21.8	" " " "	2,390 "
"	12 p.c.	" " " " "	20.2	" " " "	2,532 "
"	13 p.c.	" " " " "	18.6	" " " "	2,797 "

If a fire is at its best and part of the load is taken off, the present-day practice is to lower the damper and so minimise the rate of combustion, but the effect is serious from an economical point of view, as the heat of the fire rushes into the boiler due to the lower temperature of the latter, and thus reduces quickly the temperature of the fires, so that when the load is put on again comparatively cold fires are found, and these, when stoked, being below the gas ignition point, give off black smoke. Three minutes' smoke wastes 1 per cent. of the coal used per hour.

During my series of lectures in Wakefield, I suggested to the audience one night that a present-day need in the direction of economy was a movable bridge for the furnaces, to enable the quality of combustion to be maintained, so that the length of the fires could be kept suitable to the steam demands, and one of the class tackled the subject, and a model of his now patented device is here for your inspection.

In another invention of recent date for tank boilers, the details of construction I

am not yet conversant with, but the fact of heating the air before it enters the furnace must of necessity be an economy, and one of the best aids in preventing the formation of smoke.

For many years I have studied the problem, why a tank boiler was so inefficient, as in some cases we have seen the boiler is practically dependent on the economiser. Especially does this happen when the air supply is much too high and more so when the coals used have a big proportion of hydrocarbons (gas).

In an attempt to assist in the direction indicated, a patent has recently been taken out for fitting up a furnace in such a way that a big proportion of the convected heat is transformed to radiant heat, and by this arrangement I think the actual boiler efficiency can be increased 8 per cent. or ten per cent.

It may interest many here to know that 27 years ago, Mr. Michael Longridge carried out some tests with a 30' 0" x 8' 6" Lancashire boiler, and by reducing the grate area from 42 to 35 sq. ft. when burn-

ing 35 lbs. of coal per sq. ft. of grate, the overall efficiency of boiler and economiser was 76 per cent.

The subject of smoke prevention and its natural resultant coal economy has never been so seriously considered as at present, and it is due more to the medical faculty than to the engineer that the stand is now being made.

We engineers and manufacturers burn coal, and in doing so not only waste a large portion of it, thereby robbing ourselves and depriving our descendants of their just rights, but we create conditions responsible for our annual fogs, with their long train of losses and inconveniences, depriving our industrial towns of nearly two hours' sunshine per day, and contributing in no small measure to our high death rate from respiratory troubles. Our annual coal wastage is little short of 50 million tons.

A deputation of medical men and others visited the Ministry of Health a few days ago, and one of the facts laid before the Minister was that six days' fog in Leeds increased the infantile death rate from 50 per 1,000 to 175, and in the case of a four days' London fog in November last, the death rate in the City increased from 12.6 to 14.3 per thousand.

Smoke cannot be formed with properly proportioned furnaces, flues and chimneys, as given these and ordinary care in stoking, the furnace temperature is high enough to at once ignite the gases as liberated, and heat instead of smoke is produced.

Boilers should all be fitted with draught gauges, CO<sub>2</sub> indicators and water meters. Without them, stoking and boiler efficiency is mere guess work, and only leads to confusion. The water in a boiler should not be any higher than the working level. Remember 1" above working level in a 30' 0" x 9' 0" boiler requires  $\frac{1}{2}$  cwt. of coal extra per hour.

My final word is, we spend many millions sterling per year in providing pure water to the community, and it is quite right that this should be done, but yet, the senses of sight, smell or taste will prevent us from drinking impure water, but in comparison, we waste fully 50 million tons of coal per year in fouling the atmosphere we are compelled to breathe, and directly cause over 1,000 deaths every week with our floating and easily prevented areal sewage!

## THE FARADAY SOCIETY.

MONDAY, JULY 2.

*Determination of the Density of Charcoal by Displacement of Liquids*, by J. B. FIRTH, D.Sc., F.I.C.

In two previous papers Driver and Firth show that the sorption of liquids by various types of charcoal is only complete after many days. Further it is shown that the volume of liquid sorbed varies with the different charcoals; and also for any given charcoal varies with the different liquids.

It would appear from these results that the values obtained for the density of a given specimen of charcoal by a determination of the displacement in a given liquid would vary continuously until the sorption was complete. Again since the volume of liquid sorbed varies with the different liquids the final density values obtained would likewise vary.

In the experiments described the apparent densities of cocoonut shell charcoal and sugar charcoal have been determined after definite intervals, for several liquids.

From the results obtained the value for the density of the charcoal increases with the time of contact between the liquid and the charcoal. Further the final density value varies with the different liquids.

From the previous study of the sorption of liquids by charcoal it would appear that the rate of change in the density value, and also the final density, will be determined by the rate of sorption and sorptive capacity respectively.

Capillarity is an important factor: without doubt, the capillarity alone will not suffice to explain the present results. It is the opinion of the author that an additional force of a chemical nature, which is responsible for sorption phenomena, also operates, and is fundamental. This force varies in the different charcoals also between the same charcoal and different liquids.

In the case of benzene and water with cocoonut shell charcoal, since the density in benzene is higher than that in water in spite of the fact that the capillary forces are less in the case of benzene, it follows that the sorption attraction between the charcoal and benzene is considerably greater than that in the case of charcoal and water, and the difference between the capillary forces is more than counterbalanced. Hence it is concluded that the difference in the observed densities of charcoal in the various liquids is largely determined by the sorption attraction between the charcoal

and the liquid, and to a much lesser degree by the capillary forces exerted in the system.

A further factor which must also influence the final result is the compressibility of the liquids. The liquids in the finer capillaries are highly compressed, and the compression will vary with the different liquids.

*Concentration Cells in Methyl Alcohol*, by J. GRANT and J. R. PARTINGTON.

The present investigation was undertaken with the object of clearing up the apparent deviation from Nernst's formula. The results show that no abnormalities, such as Wilson (1906) found, exist in the case of silver nitrate in methyl alcohol, the experimental values being in quite satisfactory agreement with Nernst's formula.

The theoretical results were calculated on the formula

$$E = \frac{2v}{u+v} \cdot \frac{\text{R.T.}}{\text{N.F.}} \log_{10} \frac{\mu_1 \cdot c_1}{\mu_2 \cdot c_2} = \frac{2v}{u+v} \times 0.0002 \cdot T \cdot \log_{10} \frac{\mu_1 \cdot c_1}{\mu_2 \cdot c_2}$$

The values of  $u$  and  $v$  were taken from a paper by Jones and Rouiller. This gives the transport number of the anion of silver nitrate in methyl alcohol as 0.561 at 0° C. and 0.572 at 25° C.

The values of  $\mu_1$  and  $\mu_2$  at 0° and 25° C. were taken from Jones and Bassett (*Amer. Chem. J.*, 1904, XXXII., 409-445), and were given earlier in the present paper.

Finally the observed values of the E.M.F.'s were corrected for temperature, and their values found at 0° and 25° C. so as to bring them into line of comparison with the calculated results. The E.M.F.'s were taken as directly proportional to the absolute temperatures.

*The Law of Definite Proportions in the Light of Modern Research*, by ULICK R. EVANS.

More than a century ago, a controversy took place between Proust, who maintained that homogenous bodies had a fixed composition, and Berthollet, who believed that the composition was variable. Since the law of definite proportions occupies an honourable place in all our chemical textbooks, it may be considered that the view of Proust has prevailed, at least in the case of crystalline bodies; it is generally admitted that glassy bodies have no fixed composition. Of course, even among crystalline substances the existence of bodies

("mixed crystals" or "solid solutions") having variable composition is recognised; for instance, in sodium chloride, part of the sodium atoms can be replaced by potassium, and part of the chlorine by bromine; but the mixed crystal (Na, K) (Cl, Br) thus obtained still appears to obey the rule that the number of metallic atoms present shall be equal to the number of halogen atoms.

When we consider the case of materials built up of very small (ultra-microscopic) particles, in which the "surface layers" cannot be neglected, our ideas receive some modification; Quarteroli has calculated that ultramicroscopic crystals of iron pyrites may deviate appreciably from the proper composition FeS<sub>2</sub>. Gelatinous precipitates, such as aluminium hydroxide, will usually contain more water than corresponds to the formulæ commonly applied to them, since they contain, besides "combined" water, a great deal of "capillary" and "free" water; recently Foote and Saxton have endeavoured to distinguish between the "combined," "capillary," and "free" water by observing the behaviour of the gels on freezing.

But even if we exclude cases of this kind, and confine our attention to dry, clean crystals of normal size, various facts are met with which suggest that Proust's view must be modified. In certain regions of mineralogical chemistry we almost lose sight of the principle of fixed composition. The common mineral plagioclase feldspar, for instance, is assigned a formula



although it is a homogeneous crystalline body. Such cases, which are very common in mineralogy, are seldom considered by the advocates of the law of definite proportions.

About 1913-1914 Kurnakow, as a result of his study of alloys, advanced views which amount practically to the revival of the Berthollet doctrine. Since that time, further work on alloys has served to throw new light on this question. The object of the present paper is, firstly, to rotate the present metallographical position from a standpoint somewhat different from that adopted by Kurnakow, and, secondly, to show that Kurnakow's contention is not confined to intermetallic compounds, but extends also to compounds between metals and non-metals (*e.g.*, metallic oxides, sulphides, and chlorides).

From a study of solid solutions in alloys; oxides, chlorides, and sulphides; and the

hardness of mixed crystals, the author draws the following conclusions:—

1. Many of the series of solid solutions met with in alloys show a maximum *melt-ing-point* (i.e., a maximum *thermal stability*) at a composition indicated by a simple atomic formula (e.g., AuMg); it is customary to describe this member of the series as an "inter-metallic compound," and to regard it as the parent of the series. But in cases where there is a maximum *hardness* (i.e., maximum *mechanical stability*) at a composition indicated by a simple atomic formula (e.g., AgAu), or where there is an abrupt change of chemical behaviour (a *parting limit*), it is not at present customary to apply the word "compound." Clearly the use of the word "compound" is one of convenience; there is no definite distinction between a compound and a mixed crystal. The compound is in many cases merely a member of a continuous series of solid solutions possessing greater stability and therefore greater importance than other members; the fact that the maximum stability usually occurs at a composition expressible by a simple formula is often capable of a physical explanation.

2. Many of the oxides of those metals which possess more than one valency have a variable composition; the decomposition pressure varies gradually with the oxygen content, thus distinguishing these solid solutions from mechanical mixtures. There is a continuous series (or, according to some chemists, a broken series) of iron-oxygen crystals varying in composition between  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ ; pure  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  may be regarded as the "end-members" of the series. Likewise homogeneous bodies of variable oxygen-content occur among the oxides of platinum, iridium, nickel, molybdenum, tungsten, and possibly silver, lead, and thallium. Among the chlorides we have a series of homogeneous substances with  $\text{TlCl}_3$ ,  $3\text{TlCl}$  and  $\text{TlCl}$ , as end-members, whilst crystals of variable composition exist in sub-chlorides and sub-bromides of bismuth; among the sulphides we have a series ranging from  $\text{Cu}_2\text{S}$  to  $\text{CuS}$ ; pyrrhotite is another case of a sulphide of variable composition, whilst mixed crystals also exist in the sulphides of nickel and cobalt.

3. The cause of the maximum hardness of metallic mixed crystals at the equi-atomic composition is discussed in an appendix.

I wish to thank Mr. A. J. Berry for his kindness in giving me early information

regarding the results of his work on the oxides of thallium.

*The Formation of Anomalous Liesegang Bands*, by F. G. TRYHORN and S. C. BLACK-TIN.

When the stratified precipitates known as Liesegang bands are produced by the diffusion of an electrolyte into a gel containing a second electrolyte of low concentration, it is found in general that the distance between successive strata increases as diffusion proceeds.

A reaction has been found by Hatschek, however, which presents anomalies. This is the production of lead chromate by the interaction of lead acetate and potassium chromate or dichromate. Stratified precipitates resulted from this reaction when a 5 per cent. solution of potassium dichromate diffused into a 1 per cent. agar gel containing 0.1 per cent. of lead acetate. Under these conditions normal bands were produced for a short way below the dichromate-agar interface, the distance between successive bands increasing. As diffusion proceeded, however, a second series of bands was observed. These secondary bands formed at intervals between the normal bands, and were distinguishable from them by greater width, and the distance between consecutive members of the secondary series decreased. By varying the concentrations of the reactants and by eliminating temperature changes it was shown that the production of these secondary bands could not be attributed to any changes of concentration brought about by unequal diffusion, or to temperature variations.

The time of diffusion occupied several days, and the external factor which naturally varied over this period was the light intensity. Further experiments showed conclusively that the secondary bands were to be attributed to the variations of this factor.

The mechanism of the production of these anomalous bands was obscure. A chemical origin in the reducing action of the gel under the influence of light was ruled out on the grounds that although reduction has been recorded by gelatin and gum arabic, agar is not known to possess reducing properties. A second possible action of the light would be upon the rate of diffusion of the electrolyte in the colloid medium. This was investigated by observing the limits of diffusion, under varied conditions of illumination, of potassium di-

chromate into an agar sol free from lead acetate. No variation in the limits of diffusion could be detected. An investigation of the size of the granules of the precipitates threw no light on the mechanism of the phenomenon.

In seeking an explanation of the influence of light on the formation of Liesegang bands, several factors must be considered. In addition to temperature changes, variations in diffusion velocity or concentration, and chemical effects, a change in the velocity of crystallisation may be effected by incident light. With the exception of the last effect, these possibilities are negatived by the experiments of Hatschek. The only experimental evidence bearing on the last alternative is to be found in some results of Traütz and Anschütz, and is inconclusive.

An apparent increase in velocity of crystallisation would be caused by an increase in either of the two factors, rate of nucleus formation and rate of growth of the nuclei. Considering the work of Traütz and Anschütz, it would seem that evidence is afforded for the acceleration by light of nucleus formation in the cases of particular salts, but that there is no evidence for any effect of light on the rate of growth of the nuclei once they are formed. It will be shown later that the former effect would account for the formation of anomalous bands in the Liesegang phenomenon.

The present investigation was undertaken to determine whether the production of anomalous bands of lead chromate is a unique case, or whether the effect is a general one, and further to determine whether the influence of the light could be attributed to a change in the rate of nucleus formation in the precipitation process.

Two further examples of the production of anomalous Liesegang bands were cited in addition to the case of lead chromate in agar gels first noticed by Hatschek.

It is further shown that the substances formed in these three reactions crystallise from the respective gels more readily in the light than in the dark.

Such an effect is sufficient to explain the formation of anomalous bands in these instances, and a tentative suggestion of the mechanism of the process is advanced.

Papers read:—

*On a Relation between Surface Tension and Density*, by ALLAN FERGUSON, M.A., D.Sc.

In a paper read recently before the Fara-

day Society, Dr. Macleod has shown empirically that, for a number of unassociated liquids

$$\gamma = C(\rho_l - \rho_v)^4$$

where  $\gamma$  is the surface tension of the liquid at any temperature,  $\rho_l - \rho_v$  the difference between the orthobaric densities of the liquid and the vapour at that temperature, and C a constant which is independent of the temperature. The relation holds with considerable accuracy over a wide range of temperature, and it becomes a matter of interest to examine the exactness and the physical meaning of the relation, and especially to determine the connection of the constant C with other physical constants of the liquid.

There exists an almost endless variety of such empirical formulæ.

For the purpose of this paper the power law and the Eötvös equation are sufficient guides.

The power law is by no means so widely used as it should be.

Some little time ago, desiring a form of equation which should more accurately represent the results of experiment than the evergreen

$$\gamma = \gamma_0(1 - at),$$

I tried independently the formula next in order of complexity, namely:

$$\gamma = \gamma_0(1 - bt)^n$$

If we do not attempt to force the value of the constants  $b$  and  $n$ , but determine the values appropriate to each liquid from a few measurements of  $\gamma$  and  $t$  made at ordinary temperatures, it will be found that the value of  $b$  represents the reciprocal of the critical temperature with an accuracy comparable with that of the experimental determination of  $t_c$ .

The agreement between the observed and values calculated by a development of this, is as close as can be expected, and the author feels justified in stating that the relation between the surface tension and density of any unassociated liquid is given very fairly by the equation:—

$$\gamma = \Delta \cdot \frac{\theta_0}{M_2^2 \rho_3^{10}} (\rho_l - \rho_v)^4$$

where  $\Delta$  is a constant independent of the nature of the liquid.

URUGUAY.

TENDERS INVITED FOR LUBRICATING OILS.

The British Vice-Consul at Montevideo reports that the State Electric Light

Works at Montevideo are calling for tenders to be presented by August 22 for various lubricating oils. A copy of the specification, general conditions of tender, etc. (in Spanish) can be seen at the Department of Overseas Trade (Room 52), 35, Old Queen Street, Westminster, S.W.1.

In the House of Commons recently, Sir John Simon asked the President of the Board of Trade whether he was aware that Messrs. A. E. & E. Becker, of Howden Clough Mills, Birstall, near Leeds, applied on April 16 last to the Dyestuffs Advisory Licensing Committee for a licence to import one ton of Diamond Black P.V., and that the licence was refused on the ground that Diamond Black P.V. was available under the reparation arrangements; that the lowest price at which this dye could be supplied from reparation stock was 2s. 8d. per lb., and that this price was fixed by the Board of Trade, whereas this firm could have obtained this dye under an import licence at 2s. per lb.; and whether he would take steps to enable the British dyeing industry to obtain the best dyes at the lowest price, in order that it might not be handicapped in competing with the products of other countries.

Sir Philip Lloyd-Greame replied: The application for a licence was refused on the ground that large quantities of the dye-stuff mentioned were available in reparation stock. As regards the price charged, the ordinary procedure has been followed, and the matter referred to the Price Committee which advises the Board of Trade; but that Committee, which consists of two representatives each of the dye-users and dye-makers, has not up to the present recommended any change in the price charged for this particular dyestuff.

The Department of Mines, Canada, has issued a *Summary Report of Investigations made by the Mines Branch, 1921*.

This Report contains much information of scientific interest, especially concerning the possibilities of using the vast natural resources of this Dominion.

Brief accounts are given of the following: Coal-mont amber (Alfred W. G. Wilson). The iron industry (A. H. A. Robinson). Iron oxide pigments in Ontario (Howells

Frchette). Investigations of miscellaneous non-metallic minerals (H. S. Spence). Alkali deposits of Western Canada (L. H. Cole and F. M. MacNiven). Cretaceous shales of Manitoba and Saskatchewan: their economic value as a possible source of petroleum (S. C. Eells). Oil shales of Canada (S. C. Eells). Chemical products from natural gas (R. T. Elworthy). In the Chemical Division, the possibility of producing methanol (methyl alcohol) and formaldehyde from natural gas, is discussed by R. T. Elworthy; and chemical and physical characters of bentonite, by E. A. Thompson and A. Sadler.

In his paper, Mr. Elworthy shows the possibilities of natural gas as a raw material for chemical products of great value. This is a sufficient argument for the expenditure of time and money for the conservation and development of this natural resource. The Mines Branch laboratories are well equipped to carry out much of this work, though the successful solution of these problems will be obtained only by the widest exchange of opinions and by co-operation with the natural gas and chemical industry.

A general review of ore-dressing occupies over 100 pages. Other reports from the Fuels and Fuel Testing Division, Ceramic Division, and Road Materials Division.

The report is illustrated with photographs, drawings, and diagrams.

#### CORRESPONDENCE.

To the Editor of THE CHEMICAL NEWS.

SIR,—My attention has been called to *Science Abstracts*, No. 305, of May 25, in which an extract is given under No. 648, page 261, Micro-Telescope and Super-Microscope.

In reading this extract, I would like to point out that a very serious misstatement is made, one quite at variance with what was actually said by me. I refer to the fourth sentence, in which I am made to say that the "collector" forms an image of a microscopic object at a position of the stage of the microscope. This should read, "at a position beyond the stage of the microscope," quite a different thing altogether.

The article referred to appeared in *The Chemical News*, Vol. CXXV., pages 353 to 355, December 15, 1922.—Yours, &c.,

F. DAVIDSON.

29, Gt. Portland Street, London, W.  
June 25, 1923.

## NOTICES OF BOOKS.

*Thermodynamics and the Free Energy of Chemical Substances*, by G. M. LEWIS and M. RANDALL. Pp. XXIV. + 653. Messrs. McGraw-Hill Publishing Co., Ltd., 6 and 8, Bouverie Street, London, E.C.4. 1923. Price 25s. net.

This book contains a great deal of material, which is presented in an attractive and useful form, the main idea being to treat the science of thermodynamics so as to make it readily applicable to quantitative and numerical calculations. The authors develop a variety of methods of treatment owing to the requirements of the cases, and thus the reader will find chemical, algebraic, arithmetical and graphical treatments, which should be helpful to him.

The book is up-to-date. For example, the entropy of "electron gas" is indicated, also the thermal ionisation of metals. Saha's work in connection with stellar spectra is briefly noted. On page 464 the atomic entropies per gram-atom of 76 elementary substances are tabulated. Carbon (diamond) has the lowest numerical value, while iodine, xenon, caesium, mercury and niton, as gases, are almost equal to one another, and they have the highest values listed.

The applications of thermodynamics to chemical reactions are treated at length, and it is profitable to study these, as they may afford a means of determining the limits to theoretical yields so that, in commercial developments contemplated, errors need not be made. Thus a saving of useless expenditure may be avoided. The book should prove of great value to the advanced student and the practical worker requiring fundamental knowledge of the thermodynamics of chemical reactions, and as a work of reference and study it is a most valuable one.

As regards diction, there is a clearness of statement we admire. For example, on page 606 the authors state that "If a substance is capable of undergoing a spontaneous change, and if by this change the substance is heated so that the process accelerates itself after once starting, the substance belongs to the class of explosives." It is of interest to note here that the radio-atoms are not explosive in this sense.

There is one minor fault which we think should be observed generally in connection with books intended for reference, and that is the use of special words having a particu-

lar meaning peculiar to the author, as the reader is apt to forge their significance, and he has then to read back to find out what they mean. It should be realised that anything that saves time in reading enhances the value of a book. An example will illustrate our meaning here. On page 50 it is stated that "the deviations from whole numbers of the atomic weights of *pure* isotopes (referred to hydrogen) measure the energy changes in the synthesis of the elements." The italics are ours. Not knowing the authors' use of the word *pure*, the reader is apt to ask himself—What are *impure* isotopes? The definition, however, of pure substances and solutions is given on page 10, which shows that the authors have been thorough in their work; but still we think that a few extra words in cases of this kind would be helpful to the reader. It is true that the index is useful in this respect, but it is doubtful whether it would always be of assistance.

*The Chemistry of the Inorganic Complex Compounds*, by DR. ROBERT SCHWARZ. Authorised Translation by LAWRENCE W. BASS, Ph.D. Pp. X. + 82. London: Messrs. Chapman & Hall, 11, Henrietta St., Covent Garden, W.C.2. 1923. 8s. 6d. net.

The fact that numerous double salts and complex inorganic compounds have been prepared, which do not easily accord with the simple conceptions of valency as originally defined, has led numerous authors to extend and alter these conceptions.

Probably the greatest advance in this direction is that of Werner, who put forward in 1908 his Co-ordination Theory to account for the existence of double and complex salts, basing his theory on some classical researches on the Cobaltamines, etc.

His volume, *Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie* (the second edition of which was translated into English by Hedley, 1911), gave a full account of the co-ordination theory, but possesses the disadvantage, from the students' viewpoint, of being difficult to follow. It is for such students that Prof. Schwarz has written this present volume, which is intended as an introduction to the study of complex inorganic compounds.

It is shown how the valency theory, which hold for the explanation of the formation and behaviour of all simple chemi-

cal compounds, does not hold for compounds of higher order, *i.e.*, compounds formed by the union of two or more saturated molecules.

These are divided by Prof. Schwarz into *addition compounds* and *penetration compounds* (Einlagerungsverbindungen). The former include true double salts, like  $K_2PtCl_6$ , cobaltinitrites, etc. Such substances as the metal ammines and hydrated salts are examples of penetration compounds.

The book concludes with a useful historical survey of the subject, and constitutes a further interesting contribution to the literature of this subject.

*Electrons, Electric Waves, and Wireless Telephony*, by J. A. FLEMING. Pp. VIII. + 326. The Wireless Press, Ltd., 12 & 13, Henrietta Street, Strand, London, W.C.2. New York, Sydney, Melbourne, Madrid, Genoa, and Amsterdam. 1923. Price 7s. 6d. net.

Addressing ourselves particularly to chemists, they will find in this book that Wireless is not so far removed from chemical problems as they might suppose. Prof. Fleming devotes a considerable portion of his book to atomic theory. Much fundamental science whether, for example, it be the chemical reaction, the dynamo, or the thermionic valve, as used in wireless, have in common one agent of great and wonderful activity, namely, the electron. In this book the reader will find many scientific lines of research and study blended in a most fascinating manner. We cannot do better than list the main contents:—Surface waves and wave production; waves in air; architecture of atoms; electro-magnetic fields, forces and radiation; production and detection of long electric waves; telephony and speech transmission; principles of wireless telephony; index.

As a striking instance of the practical side which is evident throughout the book, the following, from page 305, will serve as an example:—"A still more important improvement, however, has come from the United States, in the form of a thermionic valve, of which the greater part of the bulb is formed of sheet copper. The copper not only forms part of the bulb, but also constitutes the anode cylinder, and can be kept cool by cold water. The foundation of this improvement is the technical discovery of a method of sealing copper to glass in such fashion that it does not crack away on cooling or subsequent heating. The reason the

expensive metal, platinum, has hitherto been used for wires which must be sealed airtight through the wall of the glass bulb is that it possesses three essential qualities for this purpose. First, it has nearly the same coefficient of expansion with heat as lead glass. In the second place, hot platinum is "wetted" by molten glass; that is, it sticks to it; and lastly, platinum is not oxidised when heated in a blowpipe flame, but retains a bright and clean metallic surface. No other metal has been found which possesses all these properties, but the discovery was made some years ago that if copper is kept unoxidised in a flame containing reducing gas, it is, when very hot, "wetted" by molten glass, which sticks to it. Copper, however, has not the same coefficient of thermal expansion as glass, and the only way to attach a copper tube to a glass tube of the same size is to give the copper a sharp knife edge. If, then, a sort of copper thimble is made, closed at one end, but with the edge of the open end made sharp like a knife, this thimble can be sealed airtight to a glass tube of the same diameter as the thimble, and the joint will not crack away in cooling, and can be made vacuum-tight. The glass tube terminates in a re-entrant portion through which are sealed wires, to which are sealed the wires which carry the ends of the filament of the valve and also the leading-in wire for the grid."

Much of this book will appeal to the general reader having interest in modern scientific developments. The book is not without interesting theoretical matters of fundamental importance. A short but lucid account of the quantum theory is sketched. All chemists should possess the book and study it carefully, for it makes clear many things which enter into modern chemical and physical problems.



THIS list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Latest Patent Applications.*

- 14663—Rhenania Verein Chemischer Fabriken Akt-Ges.—Production of salts of barium and strontium soluble in water. June 4.  
 14954—Urfer, C.—Synthetic production of ammonia. June 7.  
*Specifications Published this Week.*  
 198287—Barnes, E. A.—Method of manufacturing fulminate of mercury.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3300.

## SULPHUR DYES.

By R. F. HUNTER, F.C.S.

The first of this important class of dyes was prepared by Croissant and Bretonniere in 1873 by heating various kinds of organic matter such as sawdust, bran, straw, etc., with sulphur and alkaline polysulphides. This dye was called Cachou de Laval, and received quite a large application as a cotton dye, despite its unpleasant odour. The substance dyes cotton green and yellow shades—these on exposure to atmosphere undergo oxidation to brown shades. These brown colours are exceedingly fast, both to light and to soap.

This dye remained the sole representative of its class until some twenty years later a French chemist, Raymond Vidal, prepared the famous Vidal Black. He obtained it by fusion of sodium sulphide and sulphur with *p*-aminophenol.

The dye by far surpassed any other cotton dye of its kind, save aniline black, in fastness to light, washing and boiling with acids, and aroused considerable interest; so much so that various organic bases were fused with sulphur, and hence arose the sulphur dye industry. The extreme fastness of the first two members gave the impression that the remaining members of the family would possess similar properties, but bitter disappointment doomed this hope.

There are at present two methods of preparation employed, viz.:

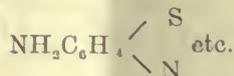
- (1) Baking,
- (2) Refluxing of boiling solution.

The latter yields the best results. The usual method of procedure is to dissolve  $\text{Na}_2\text{S}$  crystals in water, add sulphur flowers, then the base, and boil under a reflux condenser until the desired stage is reached; then filter, wash and dry. The process must be watched, since sulphur dyes, it should be remembered, are complex condensation products, and if heating is carried too far, weird results appear. During the reaction, torrents of  $\text{H}_2\text{S}$  and  $\text{NH}_3$  are evolved, and hence the preparation should be carried out in a good draught.

Very little is known as to the chemical constitution and composition, even of the

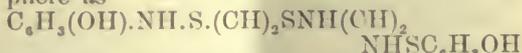
sulphur dyes, and we can only surmise that they probably contain a large number of thiazine rings and possibly mercaptan groups.

Blue and black dyes are usually derived from thiodiphenylamine, whilst yellow and brown are obtained from thiazoles. Immedial yellow is produced by fusion of dehydrothiitoluidin with sulphur, and probably consists of complex mixture of the higher primulins.

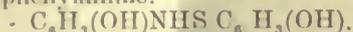


The red type of dyes are mostly unsatisfactory, and are derived from azines, and have been shown to contain an unchanged azine ring.

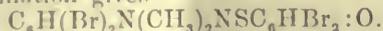
Vidal regarded his black from atmosphere as



and further by carrying out the reaction at a lower temperature he obtained dehydrothiodiphenylamine.



Immedial pure blue on oxidation and bromination gives



(tetra bromodimethyl aminothiazine).

The formula



has been assigned to Immedial Indone obtained from a mixture of *o*-toluidin and *p*-aminophenol.

A point worthy of note is that Green, by oxidising a mixture of *p*-diamine or *p*-amidophenol with a large excess of  $\text{Na}_2\text{S}_2\text{O}_3$  and solid  $\text{K}_2\text{Cr}_2\text{O}_7$ , obtained di or tetra sulphonic acids.

A few of the commoner sulphur dyes might now be described:

*Immedial Yellow* is prepared from  $\text{Na}_2\text{S}$  and *m*-tolylene diamine. If heating is carried too far, orange shades result.

*Thional Brown* is prepared by condensation of arylamino derivatives of *b*-naphthoquinone with sodium polysulphide, temperatures 240-280° C.

*Cotton Brown* is obtained from nitro diphenylamine and sodium polysulphide.

*Eclipse Brown* is made by heating tolylene diamine and oxalic acid with polysulphide.

*Immedial Black* is obtained from *p*-hydro-*o*-*p*-dinitrodiphenylamine, which results from condensation of *p*-aminophenol and dinitrochlorbenzene.

*Sulphur Black T Extra* made from dinitrophenol.

*Thiophenol Black T Extra* from dinitrophenol.

*Immedial pure blue C* is made from *p*-dimethylamine *p*-hydroxydiphenylamine.

*Immedial blue C* from *p*-hydroxy-*o*-*p*-dinitrodiphenylamine.

*Immedial Indone* from the indone  $\text{NH}_3\text{C}_6\text{H}_4\text{N}:\text{NC}_6\text{H}_4:\text{O}$ .

*Indo. carbon SSF* is by far the most important blue, and is prepared from the indophenol produced by condensation of carbazole and nitro phenol.

*Italian Green* is produced by adding copper sulphate to the melt obtained from *p*-nitrophenol and sulphur (Vidal's black).

*Immedial Green* is prepared in the same manner from the indophenol. A red sulphide dyestuff is obtained from amino hydroxy phenazine.

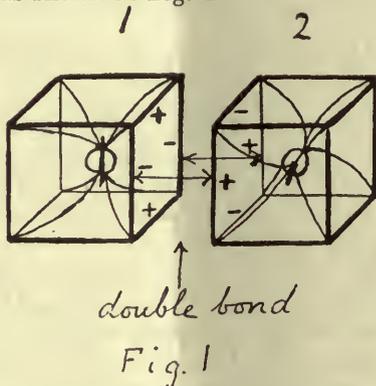
## AN EXPLANATION OF THE THEORY OF THE ROTATION OF THE ATOMIC NUCLEUS.

### Part III.

BY HERBERT HENSTOCK.

The hydrides, halides and hydroxides described in Part II. of this series were chiefly concerned with simple co-valencies or electro-valencies where single bonds came into play, and consequently did not present the difficulties which will be met with in oxy compounds, where not only double bonds, but even distortion of the octet are encountered.

A double bond might occur as described in Part I. of this series, but it might also occur as shown in Fig. 1.



Most double bonds would probably be formed in this fashion. Cube No. 1 has its nuclear poles in the plane of the paper, No. 2 has them almost at right angles to the plane of the paper. A double bond, as here shown, is composed of two positive and

two negative edges in each atom, so that when such a bond opens into a single bond it may do so at any edge.

Here the double bond is not formed on the faces of the cube, which lie at right angles to the nuclear poles, but on any of the four faces, which are parallel with the poles: as a consequence of this there cannot be more than four such double bonds operating from any atom, which has an undistorted octet.

In double bonds one or more electrons may be displaced and may occupy different corners of the octet from those which they normally occupy in the atom: the same thing will also occur in a treble bond.

Distortion of the octet will be considered here only as from the cube to the tetrahedral form, either partly or wholly as a shrinkage, but it is possible that the octet may exhibit other forms of distortion in shrinkage or expansion, as, for instance, to the octohedron. In shrinking from the cube to the tetrahedron, one or more corners of the cube disappear, leaving triangles which will constitute tetrahedral faces.

### OXIDES.

*Group I.*—General Types  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , etc., are shown in Fig. 2.

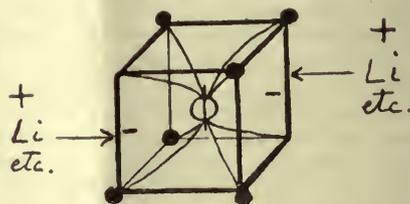
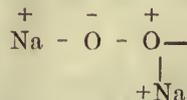
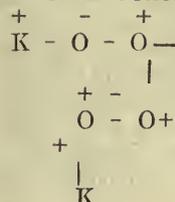


Fig. 2

$\text{Na}_2\text{O}_2$  will be constituted like  $\text{H}_2\text{O}_2$  (see Part II.) thus:—



the molecule having the same weakness in one of the oxygen atoms (Rule 2) which occurs in that compound,  $\text{K}_2\text{O}_4$  will have a somewhat similar construction, as:—



weakness. Copper is one of those elements, which may have varying numbers of electrons in its octet, see Bury (*J. Amer. Chem. Soc.*, 1921, XLIII., 1602), so that its three oxides will be constituted differently.  $\text{Cu}_2\text{O}$  will conform with Fig. 2 where it has only one electron in its octet:  $\text{CuO}$  with Fig. 3 with two electrons, and  $\text{CuO}_2$  with Fig. 5 with four electrons: its chlorides and other salts will likewise have normal structures.

Gold has similar properties to copper with respect to its octet, so that  $\text{AuO}$  will conform with Fig. 3, and  $\text{Au}_2\text{O}_3$  with Fig. 4.

The reasons for the instability of the cuprous salts and also of most of the salts of gold do not seem clear; it is possible that the cause may be due to the change in the numbers of electrons in the octets of these elements, which brings about stable or unstable arrangements in their atoms. Silver peroxide,  $\text{Ag}_2\text{O}_2$ , will probably have a composition similar to that of sodium or hydrogen peroxides, since when  $\text{Ag}_2\text{O}_2$  is

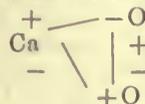
slowly acted upon by water it yields  $\text{H}_2\text{O}_2$ . The instability of  $\text{Ag}_2\text{O}_2$  is therefore accounted for.

*Group II.*—General types,  $\text{BeO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{ZnO}$ , etc., are represented by Fig. 3.

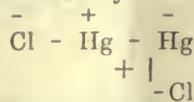
In the octet of the metal the electron at (b) has travelled from its normal position (a) and a similar action has occurred in the oxygen octet.

The stability of these oxides to heat is very great, but the bond is only stable to heat and not to the electricity of other atoms, for it is weak enough to be attacked by such a neutral substance as water, which fact is a good demonstration of the difference between the actions of these two forces.

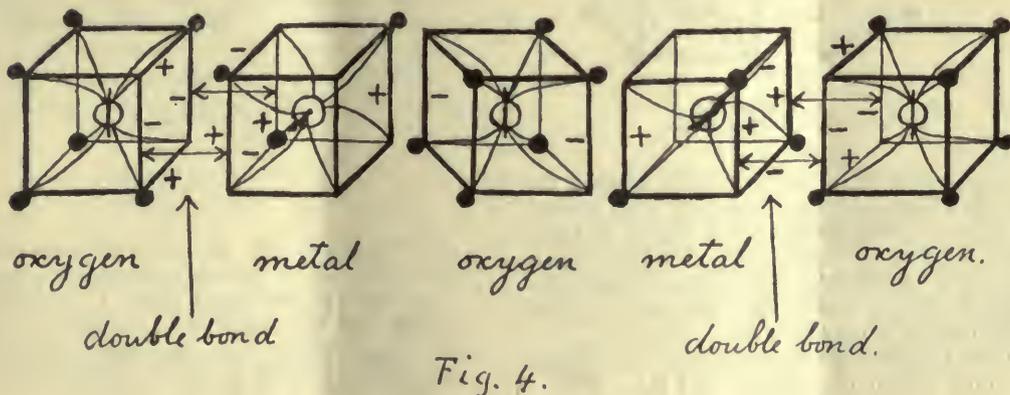
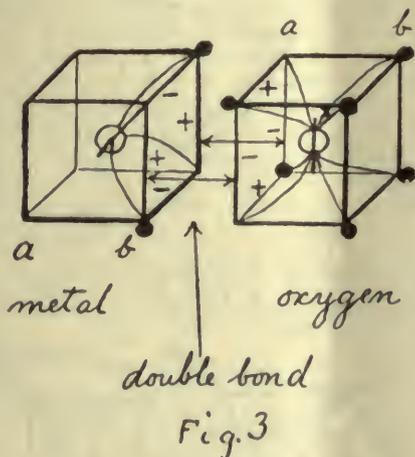
The peroxides of the types  $\text{CaO}_2$ ,  $\text{BaO}_2$ , etc., will have a somewhat analagous constitution to that of hydrogen peroxide, since they can be formed by its action upon the hydroxides of these metals: their instability is thus accounted for. They will be constituted as follows:—



Mercurous salts will be abnormally formed. Mercurous chloride, as an example, is not so stable as the mercuric salt; since its vapour density agrees with the formula  $\text{Hg}_2\text{Cl}_2$  (see Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, XXXII., 1434, and *Ann. Physik*, 1910, XXXIII., 979) it will be represented by



*Group III.*—General types,  $\text{B}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , etc., are constituted as shown in Fig. 4.



where three oxygen atoms show the same and are all quite regular.

Group IV.—General types,  $\text{CO}_2$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{SnO}_2$ , etc., are represented by Fig. 5.<sup>1</sup>

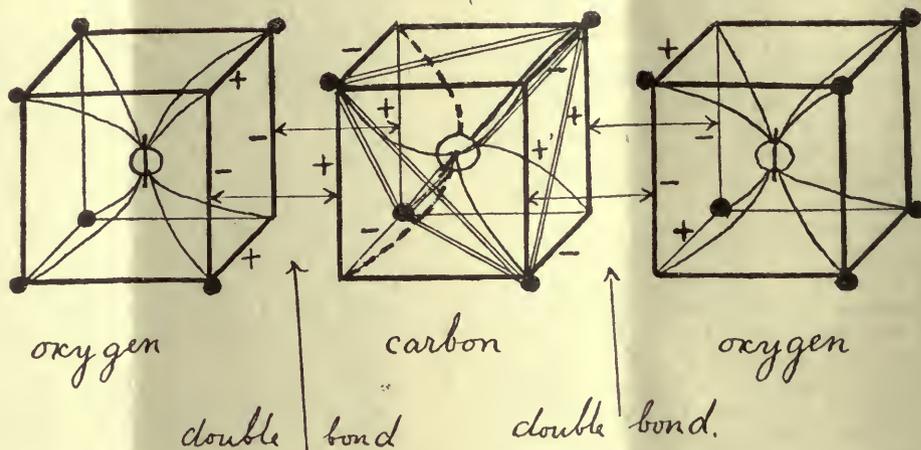


Fig. 5.

The great stability of silica is not apparent from the theory of nuclear rotation.

The case of carbon monoxide presents more difficulty than that of the dioxide, but an explanation may be found by taking into account the partial distortion of the carbon octet. If the uncombined carbon atom be taken as possessing the form of the tetrahedron and the uncombined oxygen atom that of the cube, then when two such atoms approach one another under suitable conditions for union, we should have a postulation somewhat after the manner contemplated in Fig. 6.

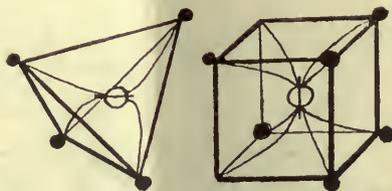


Fig. 6

There is in this case no edge or face for union, which will correspond in each atom: if, however, the carbon octet begins to form itself around the tetrahedron, but on one side only where one edge of the tetrahedron expands into a cube face, we have a state of things as shown in Fig. 7.

The dotted lines indicate the alteration in shape which the figure will take. We

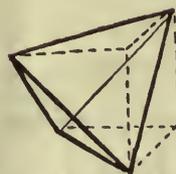


Fig. 7

can now write the complete formula of carbon monoxide as follows:—

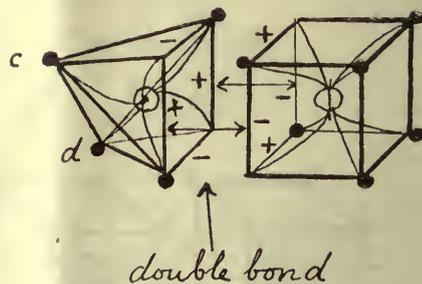


Fig. 8

There are here no free valencies in either the carbon or the oxygen atoms until the rest of the distorted cube is opened out, which would occur when another group or

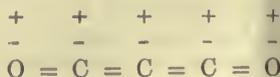
<sup>1</sup> The reason for the inclusion of the tetrahedron will appear later.

atom, say, of oxygen, came in contact with the carbon under suitable conditions for union; the result would be as shown in Fig. 5, in which the dotted lines represent the new lines of force brought into play; these pass out through the middle of the two tetrahedral faces. The tetrahedron has been retained in Fig. 5, in order to show its bearing on the whole thing. The new lines of force may be taken to be halves of the old lines of force running to the electrons (c) and (d) in Fig. 8.

When lines of force run out to the corners of the octet of an atom to positions where there are no electrons, and when no union occurs with another atom, the first atom will be in the activated or nascent condition; if union occurs, these lines of force remain in position, but when union does not take place they may shrink into the nucleus or they may coalesce with the lines of force running to neighbouring electrons, in which case distortion would occur.

This view of the matter may seem, at first sight, a little bizarre, but when it is remembered that a transition of this kind is only a passage from hemihedral to holohedral types, well known in crystallography, there seems no reason why it should not occur in such cases as this, the only difference being that it might take place in stages. It explains both the possibility of the existence of carbon monoxide, as well as its instability to certain reagents such as oxygen, chlorine, etc. (see rule 7), since the opening up of the second cube face in the carbon atom will take place more readily after the first has been formed. At the same time the double bond in CO is a normal one, and this, together with the likelihood that a small quantity of electrical energy or effort would be necessary to open up the distorted carbon octet, gives CO enough stability to exist, although only half of the normal valencies of the carbon are saturated. This substance is another instance of great stability to heat but not to the electricity of other atoms.

C<sub>3</sub>O<sub>2</sub> will be normally formed like CO<sub>2</sub>, thus:—



Each double bond is composed of both negative and positive edges, as shown in Fig. 1.

As analogous cases to CO, in this group, might be cited those of the stannous and plumbous salts. The example of stannous

chloride, which will be seen in Fig. 9, is a representative one.

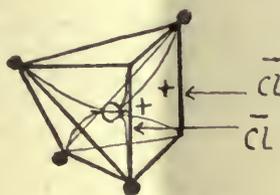


Fig. 9

This configuration explains the readiness with which the compound absorbs oxygen, since the second half of the cube is easily opened.

The tendency of the octets of the elements of this group towards distortion seems to be greater than those of most of the other groups: also quadrivalence seems to become less pronounced with increase of atomic weight, the greater number of internal electrons in the atoms of the members of higher atomic weight evidently weaken the lines of force to the electrons of their octets, thus encouraging distortion.

It cannot be thought that every atom has a full cube octet; as examples, hydrogen, the alkali metals, the alkaline earths, and the boron group have not enough electrons in their outer layers to warrant us in supposing that an imaginary cube, having only one or two corners occupied by electrons, surrounds the nucleus; these elements must naturally have *distorted* octets, and it is therefore more than likely that those elements, having larger numbers of electrons in their octets, may also exhibit distortion, even in the combined state.

Chemical Research Laboratory,  
School Gardens,  
Shrewsbury.

GENERAL NOTES.

THE STRUCTURE OF THE ATOM.

The issue of *Nature* for July 7 contains a special 16-page supplement, in which Prof. Niels Bohr, professor of physics in the University of Copenhagen, gives a comprehensive and striking account of the present state of knowledge of the structure of the atom.

Prof. Bohr has taken a leading part in the development of modern conceptions of atomic structure; and he devotes particular attention in his paper to the interpretation of spectra, and the main features of the properties of atomical elements on considerations of the manner in which an atom can be imagined to be built up by the capture and binding of electrons to the nucleus, one by one.

#### NEED FOR SETTLEMENT OF EUROPEAN SITUATION.

In the course of his speech at the Bradford meeting of the Federation of British Industries, Sir Eric Geddes said:—

“The general upward trend of trade which goes on through the centuries is, therefore, checked because of the disturbed condition of Europe, and while I see fair reason to hope for an upward trend in the cycle of trade, I can at present see nothing but blackness when I look for a resumption of the upward progression in the general level of trade shown during the last century. Therefore, as first and foremost of all measures which can be taken for the improvement of trade, and the reduction of unemployment in this country, I would put the settlement of the European situation. We, as a great exporting country, are worst hit of all by the present state of affairs in Europe. Our unemployment is caused by that, and I do not think that the working, trading, and banking community of the country can too insistently bring before His Majesty's Government the conviction which I feel—and which I believe is generally felt—that the great problems of this country would melt as mist melts before the sun, if a stabilised condition could be brought about in Europe. It is not only the direct influence on trade that is felt; but it has an influence on taxation, and taxation is one of the great burdens against trade to-day.”

In a pamphlet issued by the United States Geological Survey\* some interesting particulars are given of the occurrence of diamonds in Arkansas.

Stones found within the exposures of peridotite and have been mined to a depth of 20 feet, and the deposit is thought to extend to great depths. Dr. G. F. Kunz con-

siders that the peridotite is the source of the diamonds. The production so far does not appear to be very great, although it is stated that it is difficult to obtain complete figures of production, some 5,300 stones are known to have been obtained.

The method of separating the stones is the same as is now practised in Kimberley, viz., working the material in circular pans having a revolving vertical shaft to which radiating arms are attached, at stated intervals the concentrates are removed and passed over grease tables to which the diamonds adhere while the other minerals are washed off. The stones are said to be mostly small, and to vary in colour from white to yellow and brown, some very fine crystals have been found.

\* *Diamond-bearing Peridotite in Pike County, Arkansas, by Hugh D. Miser and Clarence S. Ross. Bulletin 735, 1.*

The current number of the *Analyst* contains a paper by H. Droop Richmond on the action of potassium carbonate upon lead glass. It was found that the apparently dry salt had an appreciable action on the glass, and that the action increased rapidly as moisture was absorbed. Both lead and arsenic were found in potassium carbonate that had been stored in bottles containing these substances, and the danger of the use of such bottles as containers for this salt is pointed out.

#### LABORATORY EQUIPMENT.

The Council of the Society of Chemical Industry have received from the Department of Scientific and Industrial Research a request to nominate three or four members to furnish information with regard to the quality and technical range of British production of optical glass and instruments, laboratory glass and porcelain, synthetic organic chemicals, analytical reagents, and other fine chemicals. The Department had already sought the opinions of a large number of professors of chemistry, physicists, and others, but appeared to have addressed enquiries to very few practitioners in chemistry. The Council suggested, therefore, that useful opinions might be obtained from such practitioners,

and they have forwarded the names of Mr. W. T. Burgess, Dr. J. T. Dunn, Dr. Bernard Dyer, Mr. E. W. Voelcker (Hon. Treasurer), together with that of Mr. H. W. Cremer, who is responsible for supplies in the chemical department of King's College, London.

The Council have also appointed a Committee to consider the proposal from the National Physical Laboratory that the work of the Joint Committee for the Standardisation of Scientific Glass-ware should be brought under the ægis of the Institute of Chemistry. The Council hold that the proposal is desirable on general grounds, but in order to obtain more detailed information with regard to the probable and possible activities expected of the Institute in this connection; they have appointed a Sub-Committee consisting of the President, with Dr. Brady, Dr. Bernard Dyer, Dr. J. J. Fox, Sir Herbert Jackson, and Mr. E. W. Voelcker (Hon. Treasurer), to confer with representatives of the National Physical Laboratory, the Department of Scientific and Industrial Research, and of such other bodies as the Sub-Committee may deem desirable, and to report to the Council on the proposition.

The Special Purposes Committee have appointed a Sub-Committee, consisting of Messrs. E. R. Bolton, O. L. Brady, F. H. Carr, P. H. Kirkaldy, and R. H. Pickard, to consider and investigate the present British production of filter paper.

## SMOKE PRODUCTION AND THE POTTERY INDUSTRY.

BY CUTHBERT BAILEY, OF THE POTTERY MANUFACTURERS' FEDERATION.

The man has yet to rise who will teach industry the means to extract full value from the coal it burns; invention after invention has been recorded at the Patent Office, but still our industrial centres lie under their black mantles.

That the past has been wholly blameless few manufacturers would contend, but bitter and costly experience has taught the wisdom of caution.

But, oblivious of past and present endeavours, there is arising a type of legislator who hesitates not to impeach every industry of reckless waste, and manufacturers generally of wallowing in content and

inaction, and who roundly accuses local governing authorities (in the words of a recent public speaker) of being "influenced too much by the selfish considerations of their manufacturing friends." These men, with their perambulating minds, with their power of generalisation and reducing masses of evidence to mere paradoxical phrases, are active to-day with an interrogative eye-glass, and, as a consequence, legislation is now proposed that threatens the very life of some of the nation's industries.

As a few years' dissipation will break the continuity of will and the sequence of intellect of any man, so would premature legislation react on industry.

Industry invites investigation — though investigation by duly qualified experts— under the sure conviction that any unprejudiced enquiry would dispel the insinuating delusions now being broadcasted.

Every industry has its essential processes and its own inherent limitations; all carry their own signals and the expert alone knows the cyphers. Of all industries the manufacture of pottery may be claimed to be the most complicated and intricate, and it is probably realised by few outside the pottery areas that the great bulk of the smoke emitted is not made in raising the necessary power to drive the machinery for its production, but is made in the various "baking" stages to which all pottery must of necessity be subjected in the process of its manufacture.

The first "baking" stage is that which reduces the formed clay to a durable and stable state such as will permit general handling, and the subsequent glazing and decorating. But the mixture of the various clay ingredients that form the final composition of the ware, after being brought to a dry state, possesses a water of combination that varies from 6 per cent. to 12 per cent. of the total weight of the articles themselves, and, as a "kiln" may contain each time it is fired from ten to thirty tons of pottery, according to the type of articles being manufactured (placed in the fireclay "saggars" that are piled up in hungs), it follows that from approximately 10-30 cwts. of water is to be dispersed during the initial stages of the "baking." This dispersal, if cracking, warping, staining, and even general collapse of the articles, is to be avoided is essentially a gradual process, and occupies the first 20-30 hours of the "baking"—and woe betide the manufacturer whose fireman unduly

expedites what is technically called this "smoking period."

Suppose an oven holds 20 tons of clay-ware carrying 10 per cent. of combined water, two tons of water is to be dispersed, which at 500° will occupy roughly one-quarter of a million cubic feet. As this rushes into the cold air outside it is naturally condensed, and, stained by the products of combustion from the burning coal, forms a cloud of what the man in the street would call "smoke." Similar remarks apply to the water in the moist goods in the earliest stages of the firing (below 200° C.) during the so-called water-smoking period—and all this steam is further supplemented by that produced by the combustion of the hydrogen compounds of the fuel itself.

During these "smoking" periods what is called smoke is, therefore, in the main, only discoloured steam; *after their completion little smoke is emitted from a modern oven.*

But smoke itself is an essential concomitant in the manufacture of the famous Staffordshire blue bricks, blue roofing tiles, and many grades of pottery. So far as our present knowledge goes it is not a mere reducing atmosphere that is in question; *decomposing hydrocarbons* are required to produce the required effect. There are further what might be called "qualities of smoke," for the results obtained with some types of smoke produce better results with than others. The old potters knew this, and in the production of lustre effects, red "sang-de-bœuf," and other types of decorative effects, one will find in the old literature that they attached a special virtue to smoke derived from particular shrubs, etc. Thus Piccolpassi favoured "the branches, etc., of green broom"; another recommended "rice husks," and so on. English Potters, under the lead of Mr. Bernard Moore, have during the last twenty years rediscovered the secrets of the old lustre glazes, and Chinese red glazes, and are to-day producing decorative effects that are universally acclaimed as surpassing in general beauty any of the works of the old potters—but *let it be realised that the one essential condition for their production is a reducing atmosphere.*

Pottery manufacturers are not indifferent to the progress of public opinion on this smoke question, but let not that opinion be formed on a mendicant truth. Essential conditions of manufacture must be conformed to; while the pressure of international competition is always sufficient

to ensure that all unnecessary waste of fuel will be constantly subjected to the closest investigation.

—*Fuel Economy Review, June, 1923.*

## BRITISH v. GERMAN GOODS IN NORWAY.

### CHEMICALS.

There is a good market for British heavy chemicals, such as bleaching powder, salt cake and soda. Good business may be done in alum for the paper trade, and there are also good prospects in aniline dyestuffs. Germany is showing signs of being unable to deliver the goods, and there is therefore every chance of a good opening for British dyestuffs. This also applies to fine chemicals.

—*Bulletin of the Federation of British Industries.*

## NEW RAPID-REGENERATING "PERMUTIT."

One of the interesting features of the Textile Exhibition at Nottingham is the exhibit, for the first time, of the new "Permutit" Rapid-Regenerating material for water softening, which marks a great advance in the technique of water purification by zeolites.

The new material is named "Permutit B." Its principal difference from the ordinary Permutit lies in the time taken for regeneration. Previously a Permutit unit was designed to soften water for 10 to 12 hours continuously. It then required an equal time for regeneration. Where day and night working was the rule, this involved the use of two units.

A "Permutit B." plant softens for a shorter period, ranging from 3 to 6 hours, and is then exhausted. It can, however, be completely regenerated and put to work in under one hour. The advantages of this are obvious. One unit only is required for day and night working, as the plant is continuously in operation except during the one-hour periods in which it is regenerated. All that is necessary is sufficient soft water storage to provide for one hour's requirements, to enable one unit to be used throughout the 24 hours.

"Permutit B." uses less salt than ordi-



nary Permutit, thus effecting saving in the cost of treatment. It will be seen that the new material brings down the cost of the Permutit process considerably, by saving one unit where continuous working is required, and by reducing the salt consumption.

Formerly the standard and universal product employed in connection with the elimination of calcium and magnesium from water by the base-exchange principle was produced synthetically, either by furnacing or by precipitation. The "Permutit" produced in this way was always subject to certain limitations.

The latest class "Permutit," which has now been in commercial service in water softening for close on three years, and which is a non-synthetic material specially treated to increase its activity, and to stabilise its qualities, has the following advantages as against all previously employed zeolites:

(1) Free carbonic acid, which exists to a greater or lesser degree in all water supplies, has no destructive effect upon it.

(2) It is to a much greater degree immune from depreciation in structure and activity by reason of iron in the water.

(3) A rate of exchange, and, therefore, a permissible rate of flow through any given plant, of upwards of ten times that of previous Permutit materials, can be effected.

(4) A similarly rapid regeneration of the material as and when the point of exhaustion has been reached at the end of a day's run, is feasible.

(5) With the new material a reduction of from 25 per cent. to 33½ per cent. in the requisite weight of salt for regeneration is effected.

(6) Lastly, and this, perhaps, may be regarded as the most important advance in the art, the "commercial" phrase of "zero-hardness" which has always been employed in regard to waters softened by the base-exchange method, is literally and actually borne out by the new material.

The new softening material is put on the market by United Water Softeners, Ltd., sole proprietors of the Permutit patents in the country.

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL INSTITUTION.

A general meeting of the members of the Royal Institution was held on July 2, Sir

James Crichton-Browne, Treasurer and Vice-President, in the chair. The death of Sir James Reid, Bart., was reported to the meeting, and a resolution of condolence with the family was passed. Mr. R. N. Lennox was elected a member.

#### THE INSTITUTE OF METALS.

##### AUTUMN MEETING.

The annual autumn meeting of the Institute of Metals will be held this year in Manchester, on September 10-13, and promises to be an exceptionally interesting gathering. The meeting will open with the second annual autumn lecture, to be delivered by LT.-COL. SIR HENRY FOWLER, K.B.E., on *The Use of Non-Ferrous Metals in Engineering*. The lecture will be a popular one, and is open to the public, tickets being obtainable from Mr. G. Shaw Scott, M.Sc., 36, Victoria Street, London, S.W.1.

The mornings of September 11 and 12 will be devoted to the reading and discussion of papers. After an official luncheon on September 11, visits will be paid to several large works in the vicinity of Manchester, and in the evening there will be a reception at the University, when the new metallurgical laboratories will be officially opened. Following the conclusion of the business side of the programme on September 12, the afternoon of that day will be devoted to a trip along the Manchester Ship Canal, and in the evening there will be a smoking concert at the Midland Hotel. A trip to Chester has been arranged for September 13, this excursion also including a launch trip up the river Dee. For those persons intending to proceed to the British Association meeting at Liverpool the same evening, the trip to Chester will be very convenient, Chester being within easy reach of Liverpool.

Reduced fare facilities have been arranged with the railway companies in connection with the Manchester meeting, and the necessary vouchers for obtaining these facilities can be obtained on application to the Secretary, Mr. G. Shaw Scott, who will be glad to send a detailed programme of the meeting to those interested.

## THE CHEMICAL SOCIETY OF JAPAN.

Papers communicated to the Society:—

*On the Quantitative Separation of Platinum and Iridium*, by SHIN-ICHI AOYAMA.

*On Contact Potentials*, by SHIRO TAKEGAMI.

*On a New Method for the Determination of Sulphur Contained in Iron*, by TERUO ASHIDA.

## THE GEOLOGICAL SOCIETY OF LONDON.

JUNE 20, 1923, PROF. A. C. SEWARD, Sc.D., F.R.S., PRESIDENT, IN THE CHAIR.

Miss P. de B. F. Bowen-Coulthurst presented a geological hammer, chisel, and satchel formerly belonging to George Bellas Greenough, first President and one of the founders of the Society. She also presented a number of valuable documents and minute-books of great historical and scientific interest, forming part of the earliest records of the Society's activities.

Dr. Herbert H. Thomas, M.A., V.P.G.S., gave a demonstration of the Source of Origin of the Stones of Stonehenge, illustrated by lantern-slides.

The following communications were read:—

*The River-Gravels of the Oxford District*, by KENNETH STUART SANDFORD, B.A., F.G.S.; with an Appendix on the Non-Marine Mollusca, by ALFRED SANTER KENNARD, F.G.S., and BERNARD BARHAM WOODWARD, F.L.S., F.G.S.; and an Appendix on the Mineral Analyses of the Clay- and Sand-Deposits of Wolvercote, by R. C. SPILLER, B.A.

A discussion followed.

*The Deposits of Paleocene Mammalia in Belgium*, by PROF. LOUIS DOLLO, Sc.D., FOR.MEM.G.S., and PROF. P. TEILHARD DE CHARDIN, D.Sc.

DR. G. T. PRIOR, M.A., F.R.S., exhibited a meteoric stone which fell at Ashdon, near Saffron Walden (Essex), on March 9, 1923.

DR. L. L. FERMOR exhibited microscopic slides of cordierite from Indian "paralavas," pleochroic in thin section, in illustration of his remarks on Dr. C. E. Tilley's paper read on June 6.

MR. K. S. SANDFORD exhibited mammalian remains and implements, in illustration of his paper.

The next meeting of the Society will be held on Wednesday, November 7, 1923.

## PETROLEUM—A SHORT HISTORY.

BY J. NORMAN TAYLOR, M.S.

Petroleum and its products are in greater use to-day than at any other time in the world's history. When we consider that at present there are millions of motor cars, hundreds of thousands of motor boats, to say nothing of a steadily increasing number of other internal-combustion engines depending for their usefulness upon gasoline, kerosene and lubricating oils, the necessity of insuring an adequate supply of petroleum is obvious. Another petroleum product, fuel oil, is being consumed in increasing quantities both upon land and on the sea. Yet, while the demand for petroleum and its products is growing, the supply of crude oil is being rapidly depleted. No wonder that our statesmen and scientists are searching for a solution of the oil problem—a situation that can only be relieved by finding new supplies, eliminating waste, and adopting improved methods in refining processes.

The increasing importance of this commodity in our national economy makes the story of petroleum a most interesting one indeed, not only to those who are pursuing the study of chemistry and the allied sciences, but to all who have contact with modern civilisation.

Petroleum is a complex mixture of hydrocarbons varying in physical state from solid to gaseous, and in colour from coal-black, through brown, greenish, red and yellow, to colourless. The chemical nature of its constituents varies with the locality in which it is found, the chain bodies predominating.

Although the petroleum industry of the United States is of comparatively recent origin, the crude oil has been known from the earliest historical period and in this

country had undoubtedly been long used by the Indians.

It occurs in rocks of all ages, "from the lower Silurian to the most recent" (Merrill), and as a rule in sandstone formations. Occasionally it is found in limestones and shales. Geologic relations indicate petroleum to be of organic origin—a product derived from the slow physical and chemical alteration of ancient deposits of vegetable and animal material under the influence of heat and pressure.

For convenience, the sources of petroleum in the United States may be classified as follows:—

The Appalachian field (centring in Pennsylvania), the Lima-Indiana field (in Indiana and Ohio), the Illinois field, the mid-continent field (centring in Oklahoma), the Gulf coast field (in south Texas and Louisiana), the Colorado-Wyoming field, and the California field. In the midcontinent field lie various pools, groups of pools, or districts, the distinguished ones being called the Cushing pool (Oklahoma), the Healdton pool (Oklahoma), the Caddo district (north-western Louisiana), and the north Texas district.

There are about as many varieties of crude petroleum as there are oil fields. However, the refiner recognises three distinct types, noted below, each of which must be handled by different methods. The paraffin base crude similar to that found in Pennsylvania and West Virginia is essentially a light-coloured crude containing paraffin; the asphalt base crude, similar to that found in Texas and California, contains no paraffin, and is generally dark coloured, almost black; mixed base crudes, similar to those found from Ohio to Oklahoma, are essentially mixtures of paraffin and asphalt base crudes. California oils contain nitrogen and ring compounds.

Professor Charles E. Munroe, in his well-known monograph on "Petroleum Refining," states that it is not surprising that petroleum obtained in Texas, California and Ohio should differ in appearance and properties from each other and from the better known Pennsylvania oil and from that obtained from other parts of the country. He attributes this difference in appearance not only to the fact that petroleum consists of a mixture of various hydrocarbons from different acyclic and cyclic series and of hydrocarbon derivatives containing sulphur or oxygen or nitrogen or other elements which themselves differ widely in

properties and appearance, but also to the varying conditions under which the petroleum is produced and to the effect due to migration.

Crude petroleum has a limited application and owes its great value to the products derived from it. It is, therefore, treated at the point of origin or is transported to an industrial centre by tank car, tank ship, barge, or pipe line. This latter mode of carriage is remarkable for its ingenuity, and we have to-day the remarkable achievement whereby vast quantities of oil are made to flow under rivers and through mountains to great refineries on the seaboard such as are found at Philadelphia, Bayonne, and Baltimore. Upon arrival at its destination the crude oil is freed from water and other sediment by allowing it to settle in storage tanks, after which it is pumped into retorts where it is submitted to fractional distillation.

This operation depends upon the principle that different liquids, at the same pressure, have different boiling points. The mixture of various hydrocarbons when submitted to gradually increasing temperature might be supposed to assume the vapour condition at the temperature of their respective boiling points and upon condensation, the individual constituents of the petroleum would be in their pure state. But such simple conditions do not obtain, since the boiling points of mixtures vary inversely as the vapour pressures. Although the composition of the vapour given off from such mixtures bears no close relation to the composition of the mixture, the vapour contains a preponderating amount of the most volatile constituent. Hence it is to be expected that when the crude oil is subjected to gradually increasing heat, the constituents are successively converted into vapour substantially in the order of their volatilities, but that the separation thus effected would not be perfect, as the oils of the higher boiling points are to some extent carried over by the vapour of those of lower boiling points.

It is evident from this that difficulties arise in the distillation of petroleum attributable to one or other of three causes: (a) to the presence of two substances, the boiling points of which are very close together; (b) to the presence of one or more components relatively in very small quantity; (c) to the formation of mixtures of constant boiling point. These difficulties have to a great extent been obviated by the use of dephlegmators similar to the Hempel column,

in which the dephlegmating column consists of a drum filled with cobble stones, surmounted by a number of tubes. A large surface is thus presented, and a more complete separation of the constituents of the crude obtained.

The distillation retorts, known as stills, are of cylindrical form, constructed of boiler plate, and are set horizontally in brick-work furnaces arranged in batteries. Stills surmounted by dephlegmators such as described above are known as "tower stills." Upon the application of heat the crude oil is converted into vapour and the vapourised oil, upon passing into the condensers, is thus brought into the liquid condition. In practice it is usual to divide the distillation into two operations, the more volatile products, naphtha and kerosene, being obtained in the first part and the residue being transferred to the tar stills and heated to a higher temperature with the object of separating the lubricating oils and paraffin. By the use of "tower stills" the entire distillation may be conducted without transfer to the tar stills, as the tower is supplied with three traps, from the first of which may be collected heavy distillate, intermediate distillate from the second, and light distillate from the third, and the still run to "maltha" or coke as desired. The streams of distillate are from time to time diverted into various tanks by the stillman. When the still temperature reaches about 325° F., the crude naphtha ceases to come over, and the stream is directed into the lamp oil tank. When that portion of the oil from which the high test oils of 120° to 150° F. fire test are prepared, is distilled off (the still temperature being about 600° F.), the fires are slackened, and if it is desired to produce a maximum amount of light products in preference to a maximum amount of the heavy lubricating oils and petroleum asphalts, the "cracking" process will be used.

The "cracking" process, whereby a considerable quantity of the oil which is intermediate between kerosene and lubricating oil is converted into hydrocarbons of lower density and boiling points, is one of great scientific and technical interest. This dissociation into simpler molecules may be brought about by pyrolytic distillation and, unless a catalytic agent is used, is due to super-heating of the boiling liquid. A considerable number of processes have been brought forward for effecting the transformation of heavier hydrocarbons into gaso-

line hydrocarbons, the most widely used one being that of Dr. Burton, in which the pressure which obtains is greater than the atmospheric pressure. Other processes operate at atmospheric pressure and some, as in the McAfee patent, use a catalytic material such as anhydrous aluminium chloride.

The products obtained on separating petroleum into its commercial fractions are usually purified by treatment successively with sulphuric acid and ammonia or soda, the lightest distillates being treated with about 5 per cent. by volume of the concentrated acid and the intermediate distillates with about 1.5 per cent. The treatments with acid and with alkali are conducted in agitators lined with lead and provided with an air blast and outlets for the spent chemicals and treated oils. These agitators hold from 50,000 to 150,000 gallons of oil at one charge. Concentrated sulphuric acid is thoroughly mixed with the oil by means of the air blast, and after settling the acid sludge is drawn off, the oil washed with water, then with alkali and finally brightened with fuller's earth. This treatment improves the colour and odour of the oil, and removes the aromatic and unsaturated hydrocarbons, phenols, tarry products, and other substances which lower its quality.

The acid sludge is diluted with water to separate the oil dissolved in it, and usually is treated to regain the acid used in the manufacture of fertilisers, or it is concentrated for re-use in the refinery. The oil which separates on treating this acid sludge is called "acid oil," and is, after appropriate treatment, used to some extent as a substitute for ichthyol.

Oils high in sulphur, like the Ohio oils, receive a special treatment devised by Frasch. The first distillation is conducted in the ordinary way, and the distillate subsequently pumped into another still provided with a mechanical stirrer and redistilled in the presence of an excess of finely divided oxide of copper, the contents being kept thoroughly mixed by the revolving apparatus. The second distillate is practically free from sulphur, and is treated in the usual way with acid and alkali. The residue in the still, consisting of a mixture of tar and copper oxide, is drained and pressed and the pressed copper compound is revived through roasting and used over again.

The residue from the kerosene distillation is worked up into lubricating oil and para-

fin by distilling with superheated steam to prevent dissociation of the hydrocarbons. This steam distillate is then treated with successive portions of sulphuric acid and of alkali, then cooled by passing through a tubular cooler, when the paraffin crystallises out and is separated from the oil by means of filter presses. Both the lubricating oil and paraffin are further refined by filtering through fuller's earth or animal charcoal.

Petrolatum (known also as cosmoline and vaseline) is obtained by the careful distillation of selected grade petroleum carried on in vacuum stills. Liquid petrolatum may be prepared from the lubricating oil of fraction of certain oils and is composed essentially of the naphthene hydrocarbons.

A large number of physical and chemical tests are applied to the raw materials and manufactured products. The determination of the specific gravity is one of the tests that is considered important in every product from the lightest to the heaviest. This is generally determined by means of the hydrometer and is expressed in degrees Baumé.

The specific gravity and range of boiling points are the tests chiefly applied to the light petroleum products, some of which are commercial "pentane," used extensively as a standard of light in photometric work; petroleum ether and ligroin, both of which are used as solvents for fats, oils, waxes, and certain resins; 70° gasoline; deodorised naphtha; stove naphtha; varnish makers' and painters' naphtha, and motor spirit. The boiling point limits of these light products are being extended from time to time, so that it is impossible to define them accurately.

Kerosene is examined as to colour, odour, flash point and fire test, as well as to burning quality, viscosity, composition (as ascertained by fractional distillation) and sulphur content. The flash point is determined for the purpose of ascertaining the inflammability of the oil. There are several instruments in use for this determination, chief among them being the Abel tester, Savbalt's electric tester, Tagliabue's open and closed cups, the Elliott cup, and the Bureau of Mines tester.

Lubricating oils are of great variety, and the requirements vary with the purpose for which they are used. All should have high burning points. Viscosity is the most important index in evaluating a lubricating oil

and for those used in internal-combustion engines the "carbonising number" is a valuable consideration. The "chill," or temperature at which solid hydrocarbons are deposited, is also important.

Petrolatum and paraffin are examined principally for their melting points. Petrolatum is used extensively as a basis for ointments. Liquid petrolatum is used as a laxative and as a vehicle for substances used in the treatment of mucous membranes. Paraffin is used for a number of purposes, as in the arts and in the manufacture of candles, and is sold in several grades. The tarry residual products, certain types of which are sometimes called "maltha," are used extensively in road building. Petroleum coke is used for fuel, but since it contains very little ash and much "fixed carbon," it is used more extensively in the manufacture of electric light carbons.

These are but a few of the products which petroleum is furnishing us to-day. Upon the establishment of this industry only a few generations ago, the main product was illuminating oil, and remained so for three decades. Materials, such as gasoline, fuel oil and lubricating oils, which were then considered as by-products—in the sense that by-products are defined by Professor Munroe, namely, as "substances or results obtained in the operation of a specific process in addition to the result mainly sought"—have since risen to the rank of main products. To-day, petroleum by-products are counted by the hundreds, and are increasing in number and in importance, and it seems quite likely that the romance of the coal-tar derivatives industry will, in the not-distant future, be paralleled by a great chemical industry having its basis in petroleum.

—Abstract from "The American Journal of Pharmacy," 1923, XCV., 292-298.

#### LITERARY INTELLIGENCE.

An important new book entitled *Clouds and Smokes: the Properties of Disperse Systems in Gases*, will shortly be published by Messrs. J. & A. Churchill. The author is Dr. W. E. Gibbs, Chief Chemist to The Salt Union Ltd., Liverpool. There will be about 30 illustrations.

The investigation of matter in a highly

dispersed or "colloidal" condition has been largely directed towards those disperse systems in which the dispersion medium is a liquid or a solid. Less research has been made in fog, smoke, flame, cloud and the atmosphere itself. They are disperse systems in which a liquid or a solid substance exists in a highly dispersed, or colloidal, condition in a gas.

The author describes the various ways in which such disperse systems in gases can be formed, and deals fully with their mechanical, thermal, optical and electrical properties, and the conditions which determine their stability. This information is then applied to the practical problems of meteorology, fume condensation, gas filtration, the manufacture of substances in a finely powdered condition, and the use of smoke in warfare.

#### NITROGEN AND OTHER SUBSTANCES IN RAIN AND SNOW.

By JOHN H. WOHLK.

It seems important to gain a knowledge of the various substances that come down in the rains and snows on account of the agricultural and hygienic significance. Similar work has been carried on for some time in the chemical laboratories of Cornell College, and in many other places.

Our special purpose is to determine the amounts of nitrogen compounds, chlorine and sulphates in the rains and snows of this locality.

The work was carried on under ordinary laboratory conditions. There is included a period of eight months, October 1, 1922, to June 1, 1923. The samples were collected in two granite pans, each 20 inches in diameter. The place is an open space near the centre of Mount Vernon, Iowa, which, including the college, has a population of about 2,500, without manufacturing enterprises. This condition eliminates excessive smoke contamination of the atmosphere. In the work every possible precaution was taken to avoid contamination. The samples were always collected soon after the precipitation, and the determinations were made as soon thereafter as possible.

Altogether forty-one samples were analysed, of which twelve were snow and twenty-nine were rain. There were 70 inches of snow and 11.2 inches of rain. This represents 17.21 inches of rain considering twelve inches of snow the equivalent of one inch of rain.

We found in the aggregate of the precipi-

tations 20.35 pounds of chlorine, 0.57 pounds of sulphate as  $\text{SO}_3$ , and 3.93 pounds of nitrogen per acre. Phosphates were sometimes found, but only as a trace, never in sufficient quantity to be determined.

Expressed in parts per million, the chlorine varies from 3.54 to 28.1. The precipitations in this section, both the rain and snow, seem to come from the east, and the salt particles doubtless come from the Atlantic Ocean. The spray on the shore may be caught by the wind and is borne across the continent, until it descends, in solution in the precipitations. The chlorine was determined with hundredth normal silver nitrate, using neutral potassium chromate as the indicator.

The total nitrogen shows an average of 0.896 parts per million, and is quite constant. Electrical storms seem to have been responsible for some of the higher averages.

The average parts per million of free ammonia is 0.34, albuminoid ammonia 0.264, nitrogen in nitrates 0.346 and in nitrites 0.397, and sulphates,  $\text{SO}_3$ , 0.147.

The amount of the precipitation determines largely the number of pounds of nitrogen supplied per acre; but an examination of the pounds of nitrogen supplied by each of the 41 precipitations reveals quite a variation. This is due to the difference in the amount of rainfall, namely, 0.05 of an inch to 1.8 inches, and it shows a marked degree of concentration in the smaller precipitation. The same standard reveals the fact that during continuous precipitation, such as occurred from November 5-27, the total nitrogen gradually diminished.

We determined the various substances in each precipitation on the basis that one inch of rain on an acre weighs 226,875 pounds.

We desire to express our thanks to Dr. N. Knight for aid and encouragement in carrying on this work.

*Cornell College,  
Mount Vernon, Iowa.  
June 27, 1923.*

#### THE PROSPECTS OF A REVIVAL IN TRADE.

I think the President of the F.B.I., addressing the members in Bradford at the present time, could hardly choose any subject for his address other than the condition of trade and its prospects.

TWOFOLD MEANING OF "TRADE EXPANSION."  
An examination of the trade figures of the country over the past century, shows

two main features. Firstly, that trade moved in cycles of from 5 to 10 years; and, secondly, that trade as a whole moved steadily upwards, that is to say, that the lowest points and the peaks of the cycles of trade consistently showed a general upward tendency. The years of war upset both the regularity of the cycles and the regularity of their upward progression. At the present time, so far as I can see, in spite of the handicaps which the aftermath of war has left us, we are emerging from the bottom of a cycle, and even in spite of those handicaps I think that a mild form of optimism is possibly justified. It is difficult to account for the cycles in trade, but probably the principal reason is this. Finished goods take some time to produce, and the manufacturer looking ahead has to prophesy as to the results of his sales. As a rule a Sales Department is a little optimistic—if they were not they would not be a good Sales Department—and the manufacturing power of the country, anticipating the demand several months hence, tends to over-produce; that is to say, to produce more in prospect than the realised consumption. Free and unemployed money is used to finance this manufacture, and a point is reached when the over-production begins to show, and money becomes dearer because there is a shortage of money out of employment. Then the trade slump begins; prices break on account of over-production; manufacturers cut down their mill specifications; bankers, short of free cash, raise their credit rates; lack of confidence creeps in, and the trade depression is established. Consumption overtakes production, dear money means liquidation of stocks, and trade only begins to improve when, owing to conservative production, consumption has again exceeded it.

#### HOW TO PREVENT CYCLICAL FLUCTUATIONS OF TRADE.

It is difficult for anyone to dogmatise in these matters, but I hold the view that the cyclical depressions and heights of trade are really the outcome of the psychology of the manufacturer and the banker, but principally of the manufacturer. Without optimism and hope, this world would be a poor place, and we would effect little, but, as I see it, the principal cause of the cyclical fluctuations in trade—which are very undesirable—are caused by lack of accurate knowledge as to what the world can consume. It would be idealistic to hope that in this imperfect and competitive world we could estimate exactly what we could sell,

partitioning the demands among the various producers, but I feel sure much can be done by the collation and collection of information by the great trade and industrial organisations, to enable their members to forecast more accurately what the demand will be, and what production will be. In this, I think, the great nation of the United States of America is probably ahead of us.

#### NOTICES OF BOOKS.

*Über Naturprodukte*, Festschrift zum 70. Geburtstage MAX HÖNIG, Herausgegeben von Prof. Dr. B. M. MARGOSCHES und Priv. Doz. Dr. W. FUCHS. Pp. X. + 181, with 7 figures and a portrait. Dresden and Leipzig: Verlag von Theodor Steinkopff. 1923. Price 4s. 4d. unbound.

The recent celebrations of the Jubilee of Prof. Max Hömig by his colleagues, friends and students of the German Technical Institute at Brunn (Brno) have led the promoters to publish this collection of papers by various authors under the title of a chemical treatise on the knowledge and valuation of different natural products.

This Jubilee volume includes the contributions communicated on the occasion of the celebrations. Many were naturally from Hömig's students either still working at the Deutsche Technische Hochschule, Brunn, or in other countries.

Mr. C. F. Cross, F.R.S., communicated the first paper, *On Cellulose with Reference to Systematic Chemistry and Natural Science*.

Drs. Fischer and Tropsch, of Mulheim, gave a contribution, *Comparative Distillation in vacuo of Cellulose, Lignin and hardened Wood*.

Prof. P. Klason, Stockholm, described *Synthetic Researches on the Lignin of Pine-wood*; Prof. E. Hügglund, *Lignin Hydrochlorides*; Dr. K. Kürschner, *The Pectosan Content of Pine Lignin*; Dr. B. Elsner, *The Methylation of Natural Products*; P. Ehrenstein, *Hönig's Extract as used in Tanning*; Prof. E. Jalowetz, Vienna, *The Baking-Power of an old Wheat Flour*; F. Tempus, *The Quantitative Estimation of Starch*; Prof. Margosches and Dr. F. Steindler, *On the Hindering of Reduction by Reducing Sugars caused by Trichloroacetic Acid*; Dr. O. Wohryzek, *Raw-Sugar Refining*; Prof. E. Zerner, Vienna, *The Oxidation of Stearic and other Acids with Oxygen*; Prof. J. Marcusson, Berlin, *The Hömig-Spitz Procedure for separating Saponifiable and Unsaponifiable Oils*; Dr.

W. Fuchs, *The Humic Acid Problem*; P. Stamberger, Budapest, *Synthetic Humic Acids*; Prof. A. Lissner, *The de-sulphurising of Coke*; Prof. E. Donath, *Estimation of the Combustibles in the Firing-residues of Coals*; H. Rath, *The Hönig-Spitz Estimation of Boric Acid*; Dr. A. Kurtenacker, *Estimation of Bismuth in Ores and Industrial Products*; F. Abt, *The Purification of the Water of Brünn*; Prof. G. Ullrich, *The Water conditions in the Textile Industries of Brünn*; O. Kyas, *The Technique of Manuring Experiments*; Prof. C. Frenzel and Dr. E. Klarmann, *Röntgen Rays and their Application in Chemistry and Technology*.

The volume will appeal especially to those who have been connected, in some way, with Prof. Hönig or his work.

#### BOOKS RECEIVED.

*Supplementary Notes on Gravimetric Analysis for Beginners*, by W. Lowson, B.Sc., F.I.C. Pp. 54. 1923. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 2s. 6d.

*Summary Report of Investigations made by the Mines Branch during the Calendar Year ending December 31, 1921*. Pp. 346. 1923.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 15634—Chemische Fabrik vorm-Sandoz.—Manufacture of cardiac glucoside of bulbus scilla. June 15.  
15645—Perceira, H.—Process for manufacturing perylene vat-dyes. June 15.

- 15644—Perceira, H.—Process of manufacturing aminoperylenequinones. June 15.

#### Specifications Published this Week.

- 198385—Nielsen, H., and Laing, B.—Manufacture and utilisation of formic acid.  
198423—Wild, R., and Wild, A. H.—Manufacture of ferro alloys, particularly ferro-chromium alloys.  
198545—Hechenbleikner, U., and Oliver, T.C.—Treatment of acids.  
198576—Elektrizitätswerk Lonza.—Manufacture or preparation of metaldehyde.  
198615—Chemische Werke Altstetten Akt-Ges.—Process for the manufacture of 1-phenyl-2,3-dimethyl-4-dimethylamino-5-pyrazolone.

#### Abstract Published last Week.

- 196672—2,4-Diamidophenol; photographic developers.—King, O., of 35, Russell Road, Kensington, London.

A compound of 2,4-diamidophenol with tin chloride, of good keeping qualities and suitable for use as a photographic developer, is prepared by treating 2,4-dinitrophenol with sufficient tin and hydrochloric acid or by boiling 2,4-diamidophenol with stannous chloride and hydrochloric acid, and precipitating with concentrated hydrochloric acid; the product may further be dissolved in water, sulphur dioxide passed in, and a product containing sulphur dioxide in addition to the tin chloride obtained.

#### Abstract Published this Week.

- 196431—Organic-mercury compounds. — Wolkamp, M. E., of 1116, 2nd Avenue, Oakland, California, U.S.A.

Mercury derivatives of aurintricarboxylic acid and alkali salts thereof are obtained by heating with mercury compounds a solution of an alkali salt of the acid, or a suspension of the acid in a solution of sodium chloride. The products, which may contain one, two, or three atoms of mercury in the molecule, are substitutes for mercury salicylate; the free acids are insoluble in water, but soluble in sodium chloride solution. According to examples, products containing sodium chloride are prepared by boiling aurintricarboxylic acid with sodium bicarbonate, mercuric chloride and water, filtering, and evaporating; products not containing sodium chloride are obtained by replacing the mercuric chloride by mercuric oxide, the mercuric aurintricarboxylates being precipitated by acidifying with sulphuric acid.

Messrs. Rayner & Co. will obtain printed copies of the published specification and abstract only, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3301.

## NOTE ON THE CHEMISTRY OF HAFNIUM.

By G. HEVESY.

The near relation between the chemical properties of hafnium and zirconium is clearly exhibited by the fact that all zirconium minerals contain hafnium, in an amount varying between 1 to 30 per cent. of their zirconium content. The relationship between hafnium and its higher homologue, thorium, on the other hand, is much less conspicuous. The most typical thorium minerals, such as orangite, thorite, and thorianite, were found to be free from hafnium.

The above conclusions, drawn from geochemical data, were fully confirmed by comparing the chemical properties of the principal zirconium and hafnium compounds. This investigation included compounds with hydrochloric, hydrofluoric, nitric, sulphuric, oxalic, carbonic, phosphoric and salicyelic acids, etc. Attempts to achieve a separation of hafnium from zirconium, based on the different solubility of the corresponding compounds, showed that the most successful method of separation was by the crystallisation of the potassium double fluoride. This compound can, as is well known, easily be prepared by melting the zirconium mineral with potassium hydrogen fluoride. The zirconium and hafnium double fluoride is then extracted with the aid of boiling water, which dissolves as much as 25 per cent. of  $K_2ZrF_6$ . When cooling down the solution the greatest part of the salt crystallises out, the solubility at 20° amounting only to 1.85 per cent. (in one-eighth normal hydrofluoric acid solution). The solubility of the hafnium double fluoride (amounting to about 3 per cent.) being larger than the solubility of the corresponding zirconium compound, the hafnium concentrates in the mother-liquor. The efficiency of this method is shown by the following data:—

1000 grams of  $K_2ZrF_6$ , containing 6 per cent. of  $K_2HfF_6$ , were crystallised from a 10 per cent. HF solution. After repeating this operation four times the remaining 750 grams of the double fluoride contained only 2 per cent.  $K_2HfF_6$ , and the hafnium con-

centration of the mother liquor was correspondingly raised.

The above-mentioned method of separation can also be replaced by a crystallisation of the corresponding ammonium compound or successfully combined with the partial precipitation of zirconium hafnium compounds with ammonia, or by boiling the solution with sodium thiosulphate, and so on. Hafnium being more basic than zirconium, the first precipitate accordingly contains relatively less, the last relatively more hafnium than the original material.

The phosphate of hafnium, on the other hand, was found to be appreciably less soluble in concentrated acids than the phosphate of zirconium, but this method of separation was rather tedious considering the difficulties attending the resolution of the phosphate. A partial separation was further achieved by distilling the tetrachloride at about 250° C., but this method also was found much less successful than the crystallisation of the double fluoride. The hafnium content was in all cases Röntgen-spectroscopically determined. A detailed description of this method by Dr. Coster will be given in a subsequent issue of *The Chemical News*.

By using the above described method of separation, large amounts of hafnium still containing 5 to 6 per cent. of zirconium were obtained. A preliminary atomic weight determination, carried out with the aid of this material, gave a value for the atomic weight of hafnium lying between 178.4 and 180.2. (Concerning further details of this determination, see the July, 1923, issue of the *Ber. d. deutsch. Chem. Ges.*)

The properties of  $K_2ZrF_6$  and a large number of other double fluorides were investigated in detail by the French chemist, Marignac, and described in a most fascinating contribution to the *Annales de Chimie et de Physique* in 1860. He purified his zirconium by crystallising the  $K_2ZrF_6$  and calculated the atomic weight of zirconium

$$\text{from the ratio } \frac{K_2ZrF_6}{ZrO_2}$$

It is of interest to note that Marignac, to prove the homogeneity of the element zirconium doubted by Svanberg and others, determined the solubility of different  $K_2ZrF_6$  fractions. No difference was found. Marignac prepared his double fluoride from a nearly colourless zircon, "presumably" from Ceylon, which was found by us to have a rather low hafnium content. The

accuracy of Marniac's solubility measurements amounted to about 1 per cent., which was not sufficient to detect the presence of hafnium in his material with the help of solubility measurements.

*Copenhagen, Universitetets Institut for  
Teoretisk Fysik.  
June, 1923.*

### THE COLORATIONS OF CERTAIN QUARTZ AND THEIR MUTABILITY

BY GEORG O. WILD AND R. E. LIESEGANG.

To the older observations on the changes of colour produced by the influence of Heat, Light, and Rontgen-rays, Doelter has recently added others. Still more may be noted.

Many reddish amethysts become colourless when heated to 500-600° C. On cooling, a yellow colour suddenly develops at about 275° C.

These stones are colourless, light yellow, light violet, brownish violet, or reddish brown. Some may be colourless with amethyst coloured seams running across. All these varieties became yellow at 500-600° C. Below this the light violet stones became brownish or reddish yellow. The others changed slightly at temperatures below 500° C., the colourless ones remained partly colourless. Many of these ambers appear exactly similar to the yellow quartz of Brazil and Madagascar. In fact, the latter became colourless when heated.

An improvement of the colour shades of amethysts by the application of short or long-waved Rontgen rays has now been attempted by us.

From the work of Doelter, the hypothesis that the change of colour, which certain characteristic minerals exhibit under the action of light, Rontgen, and the different radium rays, arises from the changing of the degree of dispersion of the admixed colouring bodies.

Doubtless, such changes in the degree of dispersion make big changes in the colour. One of us, *e.g.*, has shown that the same amount of metallic silver in a layer of gelatine can be so dispersed that this layer becomes colourless and transparent like glass or the layer becomes absolutely opaque.

Between these two extremes are all stages from light yellow, orange deep red, brown, olive, green; very deep blue can also

appear by transmitted light. From the colourless, through the yellow to the black, the size of the silver particles increases, and yet it is to be admitted that it is difficult for us to abandon Doelter's views. The colloid particles of the colouring matter can undergo coagulation in the solid crystal lattice, or in a crystal aggregate a kind of coagulation (or peptisation).

This is comparable with Zsigmondy's experiments, in which red gold sols turn to blue when electrolytes are introduced.

It is also comparable with the gel formation in aqueous albumin and cerium oxide sols under the influence of Radium Rays, as was studied by A. Fernau and W. Pauli. In the latter case, the tendency to coagulate is not hindered by the presence of protective colloids, gel-media, or by the crystal lattice structure of the body.

On the other hand, Marc's results from studies of effect of traces of special organic dyestuffs in preventing actual crystal lattice formation, point in another direction. The movement of colloid particles has been shown not to occur in gels which are not quite set, how then can the coagulation be hindered inside a solid crystal? The colloid particles, then, must be regarded as not movable.

The coagulation theory completely fails to explain this.

There are other possibilities which admit of the change of degree of dispersion in a rigid system, namely, in the case where intermediate solution comes in. For instance, silver chloride should be very finely dispersed in a gelatin gel, so that the cloudiness is very small.

When sodium nitrate diffuses with this gel a great increase of the cloudiness occurs. A part of the silver chloride has dissolved to form an intermediate solution.

The other particles of the silver chloride then increase in size from this solution. This may well occur in minerals.

The Röntgen Rays make amethyst darker but the heating makes it lighter again. Diffusion would take a long time in this medium, and the changes by heating are too quick for this. Our ultra-microscopic experiments with heated and unheated amethyst have not shown any support for the theory of the change of dispersion. The purely chemical hypothesis seem to offer the most satisfactory explanation.

*(From the Centralblatt f. Min., 1922  
XVI., 481.)*

## EMPIRE COTTON AND RESEARCH.

## £5,000 DONATION TO IMPERIAL COLLEGE.

The Empire Cotton Growing Corporation has recently been considering the necessity for organised research at the Universities and Colleges of Great Britain, and has decided to offer retaining grants to certain Universities where highly specialised research is already going on. The Cotton Corporation has offered to the Imperial College of Science and Technology, South Kensington, the sum of £1,000 a year for a period of five years from October 1, 1923, the money to be devoted to Plant Physiology and Plant Pathology in the Department of Botany. This generous offer has, we understand, been accepted by the Governing Body, and the research work will be undertaken in the new Botany Building which was recently opened by the Duke of Devonshire, and to which the Rubber Growers' Association of the City of London subscribed approximately £30,000 about two years ago. This donation is tangible evidence of the value which tropical agriculturists attach to the important research work which is being undertaken at the Imperial College, especially in connection with plant physiology and pathology under the direction of Professor J. B. Farmer, F.R.S., and Professor V. H. Blackman, F.R.S. We have no doubt that other groups interested in research work will continue to support undertakings of this character.

The United States Department of Agriculture has issued a Department Bulletin, No. 1147, entitled *Chemical, Physical, and Insecticidal Properties of Arsenicals*, by F. C. Cook and N. E. McINDOO.

This study of the chemical, physical, and insecticidal properties of arsenicals on the market was undertaken in order to gain a better understanding of them, to be able, if possible, to improve them, and to produce new arsenicals for insecticidal purposes. The results of this investigation, which was conducted by the Bureau of Chemistry and the Bureau of Entomology of the United States Department of Agriculture, are here reported.

Paris green and lead arsenate, which have been standardised and found reliable for many years, have constituted the principal insecticides used against external chewing insects. However, during the past few years, the use of calcium arsenate has steadily increased, owing in part to the discovery that it is effective in combating the

boll weevil. The manufacture of calcium arsenate, although well beyond the experimental stage in most factories, probably will not be completely standardised for several years. Because of the importance and recent large-scale production of calcium arsenate, many of the results in this bulletin deal with comparisons of calcium arsenate and acid lead arsenate.

## CHEMICAL PROPERTIES OF ARSENICALS.

Arsenious oxide ( $\text{As}_2\text{O}_3$ ), commonly called white arsenic or simply arsenic, is the basis for the manufacture of all arsenicals. Arsenious oxide is a by-product from the smelting of lead, copper, silver, and gold ores, being recovered from the flue dust and fumes. The arsenious oxide first sublimed is impure, owing to the presence of carbon and sometimes of sand. The impure oxide may then be resublimed to give a relatively pure one, consisting of approximately 99 per cent. of arsenious oxide and a trace of arsenic oxide ( $\text{As}_2\text{O}_5$ ). Between 11,000 and 12,000 tons of arsenious oxide were produced in the United States in 1920, more than half of which was used for insecticide purposes. Canada, Mexico, England, Germany, France, Japan, and Portugal produce large quantities of arsenious oxide.

There are three forms of arsenious oxide: (a) The amorphous, vitreous, or glassy form; (b) the ordinary crystalline ("octahedral") form; and (c) the orthorhombic crystalline form. The amorphous form changes spontaneously into the crystalline form on standing. The trade usually recognises two grades, the light and the heavy forms, although they are the same chemically.

The literature contains conflicting statements concerning the solubility of arsenious oxide in water. Because of the slowness with which it goes into solution, many weeks being required to dissolve even a small sample of the solid, it is probable that in all of the reported results equilibrium had not been reached. The varying percentages of crystalline and amorphous material present in the samples tested, the amorphous form being more soluble than the crystalline forms, may possibly help to account for these discrepancies.

With the exception of Paris green, the arsenites are prepared by combining arsenious oxide and the base.

As a rule, arsenates are made by the direct action of arsenic acid in solution on a metallic oxide. The arsenic acid used for

this purpose is manufactured from arsenious oxide by oxidation, usually by means of nitric acid.

#### BASES USED IN PREPARING ARSENICALS.

The oxides of lead, zinc, calcium, and magnesium are the bases most used in manufacturing arsenicals. Litharge is the commercial calcium oxide. Zinc oxide (ZnO) and lead oxide (PbO), ordinarily employed in the manufacture of zinc arsenite and lead arsenate, are more expensive than calcium oxide (CaO) and magnesium oxide (MgO) used in manufacturing calcium arsenate and magnesium arsenate.

The principal lead arsenate is acid lead arsenate ( $\text{PbHAsO}_4$ ), an acid salt, so-called because of the presence of hydrogen (H) in its molecule. It has the following theoretical composition,  $\text{As}_2\text{O}_5$  (33.13 per cent.), PbO (64.29 per cent.), and water of constitution (2.58 per cent.).

In the early procedure for preparing acid lead arsenate, solutions of lead acetate or of lead nitrate were precipitated by sodium hydrogen arsenate ( $\text{Na}_2\text{HAsO}_4$ ). The tendency is to produce acid lead arsenate when lead nitrate is used, and the more basic form when the acetate is used. McDonnell and Smith obtained acid lead arsenate of practically theoretical composition by precipitating lead nitrate or lead acetate by an excess of monopotassium arsenate. A method frequently employed in manufacturing this arsenate is to mix arsenic acid ( $\text{H}_3\text{AsO}_4$ ) and litharge (PbO) in the presence of a small amount of nitric acid. The fact that acid lead arsenate is a comparatively stable compound and is but slightly soluble in water, offers an explanation as to why it burns foliage only very slightly when properly applied.

#### BASIC LEAD ARSENATE.

The early investigators recognised "basic," or "sub," arsenate of lead, and applied the term "neutral lead arsenate" to  $\text{PbHAsO}_4$ , which is the present commercial acid lead arsenate. They also applied the term "neutral lead arsenates" to lead pyroarsenates, which are not commercial products, and therefore will not be discussed here.

Basic lead arsenate may be prepared as follows: Produce basic lead acetate by the action of acetic acid on lead or lead oxide, usually litharge. Then mix it with arsenic acid, thus forming basic lead arsenate. Basic lead arsenate may also be made by the reaction of sodium arsenate, litharge,

and nitric acid, or by the action of ammonia on acid lead arsenate. It has the following theoretical composition:  $\text{As}_2\text{O}_5$  (23.2 per cent.), PbO (75 per cent.), and water of constitution and crystallisation (1.8 per cent.). The specific gravity of this substance was found by McDonnell and Smith to be 6.86.

#### CALCIUM ARSENATES.

Pickering, in 1907, stated that calcium arsenate had already been used in the United States as an insecticide. He gave the proportions of a calcium salt and an arsenate to be united in preparing calcium arsenate, recommending the use of an excess of lime in order to produce a calcium arsenate with all the arsenic precipitated and therefore containing no appreciable amount of water-soluble arsenic.

As many of the early commercial samples of calcium arsenate contained excessive amounts of water-soluble arsenic, frequent scorching of foliage resulted from its use, thus retarding its general introduction. Since 1907, many experiments to devise a method for making a commercial calcium arsenate have been performed. It is now being produced by many American manufacturers, and its sale is constantly increasing. The quality of the commercial product has been much improved during the past few years, but its course of manufacture has not yet been standardised as has that of lead arsenate.

Dicalcium arsenate ( $\text{Ca}_2\text{HAsO}_4(\text{H}_2\text{O})$ ) contains theoretically 28.3 per cent. of calcium oxide and 58 per cent. of arsenic oxide. It breaks down easily in water, yielding a large quantity of water-soluble arsenic, and is not suitable for commercial spraying purposes.

The following simple method of preparing calcium arsenate commercially, as outlined by Haywood and Smith, calls for the direct mixing of calcium hydroxide and arsenic acid, the only by-product being water: Slake the lime to a smooth paste by using from 3 to  $3\frac{1}{2}$  times as much warm water (by weight) as lime, and allow it to stand until the lime is completely slaked. Then mix it, add the cold arsenic-acid solution at room temperature as rapidly as possible, and stir the mixture well until the liquid becomes alkaline to phenolphthalein. Lastly, filter, dry, and grind the resulting compound.

The lime and arsenic acid should be mixed in such proportion that the actual weight of calcium oxide used will be equiva-

lent to that of the arsenic oxide employed. This method produces a reasonably light (bulky) material, which is easily pulverised. The finished product should contain approximately 44 per cent. of calcium oxide, from 40 to 42 per cent. of arsenic oxide, and from 14 to 16 per cent. of water and impurities, which approaches the ratio, 4 CaO : 1 As<sub>2</sub>O<sub>3</sub>. The excess of lime is used to keep any soluble calcium arsenate from remaining in the product.

#### PARIS GREEN.

Paris green, originally used as a paint pigment, is said to have first served as an insecticide in the western United States. It is a compound of arsenic, acetic acid, and copper, known as aceto-arsenite of copper. The theoretical composition of Paris green is copper oxide (31.39 per cent.), arsenious oxide (58.55 per cent.), and acetic anhydride (10.06 per cent.)

The manufacture of Paris green, which has become standardised, may be briefly described thus: Solutions of sodium carbonate and arsenious oxide are heated together, forming sodium arsenite. Crystalline copper sulphate is dissolved in warm water in a separate container. The sodium arsenite mixture is poured into a mixing tank, the copper sulphate solution is added, and the mixture is stirred. Acetic acid is added, and after a little stirring the olive-coloured mixture becomes green. The Paris green is washed with water, after which it is allowed to settle, and all the water that can be drained off is so removed. This washing should be repeated as often as necessary to remove practically all the sodium sulphate. The Paris green is then dried. The dried product is passed through a "breaker," and finally through a fine sieve or a bolting machine. The "tailings" are mixed with the next batch of Paris green. The finely divided Paris green is now ready to be placed in containers.

The conclusions that may be drawn from this investigation are that a chemical analysis of an arsenical does not give sufficient data to judge satisfactorily its insecticidal properties, and a toxicity study alone does not show that an arsenical is suitable for general insecticidal purposes, but both a chemical analysis and a thorough toxicity study are required in order to judge whether or not an arsenical is a satisfactory insecticide.

#### GENERAL NOTES.

##### TRADE CATALOGUES REQUIRED IN NICARAGUA.

Mr. T. J. Rees, H.M. Consul at Managua, has informed the Department of Overseas Trade that although the supply of catalogues and price lists available at the Consulate is very limited, he has, nevertheless, been able to divert orders to the United Kingdom through their use. Similar conditions obtain at Leon and Granada.

The Consul suggests, therefore, that there are good prospects of increasing British trade by supplying him, and the Consular Officers at Leon and Granada, with catalogues and price lists of manufacturers of the following (among others):—

Novelties, cutlery, ironmongery, pottery and glassware, stationery, fine and pharmaceutical chemicals, patent medicines, druggists' sundries, toys, firearms, and of any other articles in general demand.

Further, should samples be supplied, the Consul would be pleased to use them to the best possible advantage.

Firms desiring to take advantage of the possibilities offered, should forward three copies (for use at the three ports named) of their catalogues, etc., directly to His Majesty's Consul, British Consulate, Managua, Nicaragua.

##### GERMANY'S TRADE AND INDUSTRY IN JUNE.

Mr. J. W. F. Thelwall, Commercial Secretary at Berlin, has forwarded to the Department of Overseas Trade a review of Germany's trade and industry during June. From the report it is seen that the month was noteworthy for a further extraordinary depreciation of the mark. On the one hand this led to a strong revival of trade, with the result that an improvement occurred in many branches of industry, *e.g.*, in the textile, leather, paper, india-rubber and glass industries. The potash, machinery, and chemical industries were also able to record better sales. On the other hand, the currency depreciation led to quite exceptional advances in prices. The wage increases in the first half of June, to 55-60 per cent. as compared with May, and in the second half of June to about 60 per cent. as compared with the first half of the month. The market conditions in occupied territory continued to develop unfavourably. The pressure of occupation became increasingly

greater. The deliveries of coal and coke did not increase in quantity, while, as regards quality, they became still worse. Coke was produced only to meet the immediate requirements of the foundries and gas-works. The coal supplies also diminished constantly. The time is not far distant, therefore, when deliveries will have to cease.

*Potash.* — The general situation in the potash industry was favourable. Sales, which had declined heavily in March and April, revived in May under strong calls from home and abroad. These calls continued throughout June. As a result, shifts which had previously been dropped were resumed, so that the works in June were, in general, fully employed. The fuel supply was adequate. The quality of the coal delivered left, however, much to be desired.

#### *Chemical Industry.*

The strong home demand was maintained owing to the heavy currency depreciation which occurred in the course of the month, and it was not always possible to carry out orders promptly. The raw material supply from abroad proceeded without interruption or difficulty.

#### *Paper Industry.*

Owing to the depreciation of the mark, the prices of paper wood rose considerably. The small quantities still available on the inland market from the last fellings fetched prices two to three times higher than those in the previous month. Inland sales increased somewhat and foreign trade continued very brisk. Production equalled that in the preceding month. The labour supply was adequate. In the paper wholesale trade the demand continued satisfactory, and the factories were again better employed.

#### *India-Rubber Industry.*

The india-rubber industry was probably everywhere very actively employed, as the home demand was very lively. A considerable clearance of the accumulated stocks was, in part, effected. Price increases were not nearly able to follow the movement of foreign exchanges. The fuel supply still caused the gravest anxiety.

### BOARD OF TRADE ANNOUNCEMENT.

#### DYESTUFFS (IMPORT REGULATION) ACT, 1920.

##### APPLICATIONS FOR LICENCES IN JUNE.

The following statement relating to applications for licences under the Dyestuffs

(Import Regulation) Act, 1920, made during June, has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee.

The total number of applications received during the month was 512, of which 393 were from merchants and dealers. To these should be added the 21 cases outstanding on June 1, making a total for the month of 533. These were dealt with as follows:—

Granted—372 (of which 328 were dealt with within seven days of receipt).

Referred to British makers of similar products—96 (of which 78 were dealt with within seven days of receipt).

Referred to Reparation supplies available—41 (all dealt with within two days of receipt).

Outstanding on June 30—24.

Of the total of 533 applications, 436, or 80 per cent., were dealt with within four days of receipt.

*Board of Trade,*

*July 11, 1923.*

### CHEMICALS REQUIRED IN U.S.

Mr. L. E. Bernays, H.M. Consul at New York, reports that a local firm are desirous of purchasing the undermentioned chemicals in England, primarily for sale in Cuba:

Ref. Pyridine.

Ammonium Carbonate, Lump and Powdered.

Castor oil of the No. 1 or medicinal grade.

Whiting (Blanco Espana).

Tartaric and Citric Acid.

Naphthalene flakes and balls.

British firms desirous of receiving further particulars regarding this enquiry should apply to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1, quoting reference 20039/F.W./C.C.2.

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### THE FARADAY SOCIETY.

A GENERAL DISCUSSION ON "THE ELECTRONIC THEORY OF VALENCY," HELD AT CAMBRIDGE ON JULY 13-14, 1923.

*Valency and the Electrons*, by GILBERT N. LEWIS.

As it is the purpose of this discussion to secure a better understanding of divergent points of view, I have chosen a few questions which seem likely to arise and which concern the application of the newer theories of valence to the problems of chemistry. I should like to express my belief that the two views of the structure of the atom, derived respectively from chemical and physical researches which a few years ago seemed so incompatible, are now reconcilable.

While Bohr, in his development of quantum theory, has accounted for the general characteristics of the periodic table by assuming groups of energy levels, of which the first may contain two, the second eight, the third eighteen, the fourth thirty-two electrons, etc., there is nothing to show why the group of two electrons and that of eight play so important a role in the outer shells. Thus the rare gases from neon to niton possess eight electrons in the outer shell, the same is true for all stable elementary ions such as  $K^+$ ,  $Al^{+++}$ ,  $S^{--}$ .

Prof. Lewis went on to discuss the electron pair as the chemical bond, nomenclature, multiple bonds, conjugation and polarisation.

*Bohr's Atom in Relation to the Problem of Covalency*, by R. H. FOWLER, M.A.

Considerable advances have been made in our views on atomic structure since the idea of nuclear structure was put forward by Rutherford in 1911. From Bohr's work the main features now seem to have been worked out.

Prof. Fowler considered the physical interpretation of covalence from a study of the hydrides of boron, sulphur hexafluoride, and the co-ordinated compounds of cobalt.

*The Nature of the Non-Polar Link*, by N. V. SIDGWICK.

No theory of the physical nature of valency can take us very far unless founded on some definite conception of atomic structure. In the remarks that follow I have assumed the truth of Bohr's theory of the atom, based on the application of dynamics (under the quantum restriction) to electrons which are held in their orbits by the balance between their mutual electrostatic repulsions and the attraction of the nucleus, and centrifugal force.

It is generally admitted that the non-polar (as opposed to the polar) link consists

in the "sharing" of two electrons between the two linked atoms. The only new assumption which I make is that the orbit of each "shared" electron includes both of the attached nuclei. This assumption has been found by Professor Nicholson to be the only one which will account for the spectrum of molecular hydrogen; and it has also been put forward by Dr. N. P. Campbell as a more or less self-evident extension of Bohr's theory to non-polar linkages. The author considered the results obtained by applying this conception to chemical facts.

There are two obvious differences between such binuclear orbits and the simple orbits of Bohr. One is that the presence of a second nucleus in the orbit makes precession of the orbit impossible, unless indeed the same orbit successively includes several nuclei. The second is that all the electrons shared by any one atom have to pass through their perinuclea in due succession, and hence their periods must agree; moreover in a chain of atoms the periods of all the binuclear orbits must be the same, or must differ rationally.

The theory explains why the groups attached, say, to a carbon atom retain their relative positions, in spite of the fact that each of the electrons holding them goes round the carbon nucleus; and these positions may be expected to have the tetrahedral symmetry which Bohr finds in the 4 orbits of an electron sub-group.

It also satisfies the condition of permitting the free rotation of singly linked carbon atoms.

#### *Co-ordination.*

What Werner calls the co-ordination number of an atom is the number of non-polar links that it is able to form. This is proved by the occurrence of optical activity among the 6-co-ordinated compounds under conditions parallel to those which hold among asymmetric carbon compounds. Werner's substances can be formulated without assuming any kind of valency other than polar and non-polar linkages, if we realise that while a monovalent group (like  $-Cl$  or  $-NO_2$ ) contributes one electronic orbit to the central atom, a group which can exist as an independent molecule (such as ammonia or water) contributes two, the nitrogen or oxygen assuming a higher valency by the loss of an electron, or, if you will, supplying both electrons for the link. If the resulting complex is an ion, its electrovalency must be added or subtracted. Thus you get a value for the number of or-

bits added to the atom in the compound, and by adding this to the atomic number you arrive at what may be called the effective atomic number.

*The Electronic Theory of Valency. Part II.—Intramolecular Ionisation in Organic Compounds*, by PROFESSOR T. MARTIN LOWRY, C.B.E., M.A., D.Sc., F.R.S.

1.—*Intramolecular Ionisation in Inorganic Compounds.*

In the preceding paper of this series I directed attention to the fact that the electronic theory of valency permits of a very wide extension of Thomson's theory of intramolecular ionisation, and that polar bonds may be detected in a large range of inorganic compounds where it has been generally assumed hitherto that the linkages are all of a non-polar or covalent type. In particular, a study of the electronic formulæ of Langmuir reveals the fact that, whilst there is usually a perfect balance between the nuclear charge of each atom and the enveloping shell of electrons, in other cases the negative charge of the shell is either too large or too small to balance exactly the positive charge of the nucleus.

2.—*Application to Organic Compounds.*

An extensive application of the theory of intramolecular ionisation to organic compounds is rendered possible by taking advantage of a more recent conception of Sir J. J. Thomson. He suggests that the reactivity of double bonds in organic chemistry may be attributed to the fact that it is easier to open the hinge between two cubical octets sharing a common face than to break the hinge which holds together two octets sharing only a common edge. This view can scarcely be accepted as an adequate explanation of the reactivity of double bonds, since fluorine is in fact far more reactive than oxygen; but if the assumption be made that the rupture of the double bond takes place unsymmetrically, so as to leave 2 L-electrons on one atom and only 6 on the other, a very suggestive system of formulæ is arrived at, in which ethylene is represented as containing a "mixed double bond," whilst acetylene can be represented in a similar way as containing a "mixed triple bond."

The theory of intramolecular ionisation can thus be extended to organic compounds, if it be assumed that double bonds can assume a form in which one carbon atom carries eight L-electrons, but the other only six, one pair of electrons only being shared. Since the former atom is

then negatively and the latter positively charged, this type of double bond may be represented as made up of one co-valency and one electrovalency.

This extension of the theory of intramolecular ionisation brings the reactivity of organic compounds into line with the well-recognised activity of inorganic ions, and makes it possible to regard all chemical action as ultimately ionic in character.

The resting forms of the molecules need not be identical with their ionised or reactive forms. Examples are given, however, of organic compounds which probably have a permanently-ionised structure, comparable with that of metallic salts. In other cases evidence is quoted to show that this condition results from a definite process of activation.

Attention is directed to several phenomena which receive a simple explanation in the "crossed polarities" of compounds which have hitherto been classed as "conjugated."

The properties of "multipolar ions" are referred to as furnishing a basis for a novel theory of tautomeric ions, and an explanation of their readiness to yield co-ordination-compounds.

*Part III.—The Transmission of Chemical Affinity by Single Bonds.*

It is shown that the reactivity of the methyl-group in ethyl crotonate is in harmony with the theory of polar double bonds. It cannot be used as a proof of the existence of polarised single bonds (polar co-valencies), since it receives a simple interpretation in terms of Thiele's theory of conjugation.

The small fluctuations which are observed in the strength of unsaturated acids as the double bond is moved along the chain may be attributed to steric influences such as those which Pickard has discovered in optically active compounds.

The fact that amino-acids are sometimes stronger than the acids from which they are derived is attributed to the acylous character of the amino-group; this is usually masked by the direct neutralising action of the basic group.

The conclusion is drawn that alternate polarities are characteristic of conjugated systems, and are not developed in chains of single bonds, where both acylous and basylous groups produce effects of constant sign.

*Remarks on Some Recent Contributions to the Theory of Induced Alternate Polari-*



*ties in a Chain of Atoms*, by ARTHUR LAPWORTH and ROBERT ROBINSON.

The deductions of the Principle of Induced Alternate Polarities put forward by Lapworth and by Kernack and Robinson, though having little superficial resemblance in some respects, are, on critical examination, found to be identical in others, and suggest very similar applications of the rule. The range of phenomena embraced by the theories is very wide, but a complete exposition of the subject in relation to reactivity, orientation, mechanism of reactions, intramolecular rearrangements, tautomerism, co-ordination, triphenylmethyl, and physical properties of substances could only be attempted in a monograph, and such a work we are engaged in preparing for publication. In broad outline the principle may be said to have developed as a common expression of such well-known rules as those of Markownikoff, Michael, and Crum Brown; in particular, the regularities observed in the course of substitutions in aromatic compounds had a specially noteworthy importance in revealing the wider generalisation. It is therefore not a little surprising to find that some recent contributions to the subject reverse the order, and, employing the general theory as a basis, proceed to point out that certain groups of facts are in harmony with the principle. For example, Fraser and Humphries (*The Chemical News*, 1923, CXXVI., 257) find that the theories may be applied to the manifold problems of orientation in the benzene series.

Lowry's theory of mixed double bonds fails to suggest any explanation whatever of the most important facts which led to the recognition of the "Principle of Induced Alternate Polarities," a few of which facts have been mentioned above, and it is inadmissible as an explanation of the Principle, since it introduces theoretical limitations where no distinctions are in practice to be perceived. There are theoretical difficulties also. The remark that a double bond in organic chemistry usually reacts as if it contained one co-valency and one electrovalency is, with its double qualification, unexceptionable, being no more than a restatement of the fact that unsaturated compounds undergo polar additive reactions.

*Octet Stability in Relation to Orientation and Reactivity in Carbon Compounds*, by ROBERT ROBINSON.

The explanation of the alternating polar effect advanced by Kernack and Robinson has apparently been misunderstood in some quarters, and further remarks on the subject may not be out of place. Two deductions from the octet theory were made, and the second was an interpretation of the mechanism of addition to conjugated systems, a precise translation in electronic terms of earlier representations by means of partial valency symbolism. Here it was shown that the  $\alpha$ - $\gamma$ -rule is in part a consequence of the preservation of octets in the intermediate atoms of the chain, and the schemes given are fundamentally identical with some of the cases presented by Lapworth in a more general form. Some time before, the writer had suggested that the residual or additional partial valencies of Thiele should be replaced by real partial valencies, which in the sum are equivalent to the normal valency, and the interest of the translation in electronic terms partly resided in the fact that it was possible only when this real partial valency theory was adopted. So natural does this suggestion appear that in several recent text-books and memoirs the theory is ascribed to Thiele, although this author did not adopt a partial valency symbol derived by splitting a normal valency, and his benzene formula was not, as many writers now assume, more symmetrical than that of Kekulé.

In connection with the first deduction from the octet theory, which concerns what may be called static alternate polarity, misconception has arisen. The octet theory was employed in a more or less symbolic fashion, making no assumptions in regard to the position of electrons or the precise significance of covalency. The views advanced are considered to be just as sound on the basis of the Rutherford-Bohr atom as on the Lewis-Langmuir atom. The essential point is that there are certain stable electronic configurations associated with individual atoms and termed for convenience octets; although if they are duplets, sextets, decets, or dodecets the argument is unaffected. The second stage is that there must be some octet-stability factor which is not wholly the outcome of the equilibrium of electrostatic forces. It should be remarked that the words stable and unstable are used in reference to behaviour in the course of reactions.

THE SEPARATION AND DETERMINATION OF SODIUM AND LITHIUM BY PRECIPITATION FROM ALCOHOLIC PERCHLORATE SOLUTION.<sup>1</sup>

By H. H. WILLARD AND G. FREDERICK SMITH.

[Contribution from the Chemical Laboratories of the University of Michigan and the University of Illinois.]

A review of the literature on the separation of sodium and lithium shows that none of the methods so far suggested is entirely satisfactory. The solubility corrections are usually large and the separation must be repeated one or more times.

Most of the methods proposed involve the extraction of lithium chloride from the anhydrous mixed chlorides of the metals involved, using an organic solvent or mixture of solvents in which the chlorides other than lithium chloride are insoluble. Another general type of procedure consists in dissolving the mixed chlorides in the least quantity of water necessary for their solution, followed by the precipitation of the chlorides other than lithium chloride, by the addition of an organic solvent or mixture of solvents in which the chlorides precipitated are but slightly soluble, a correction being applied for this slight solubility.

A full and critical discussion of the papers relating to this subject up to the year 1912 is given by Skinner and Collins.<sup>2</sup> Of the more recent work, that of Winkler<sup>3</sup> employs isobutyl alcohol in an extraction method, more than one extraction being required in each analysis. The method is tedious in operation and subject to errors, because of the number of manipulations involved. In the method of Palkin<sup>4</sup> a concentrated aqueous solution of the mixed chlorides is precipitated by the addition of anhydrous alcohol followed by ether. The

chlorides thus precipitated are filtered and the small amount remaining in solution is recovered by evaporating to dryness and extracting with alcohol and ether. The method is an improvement over the others, since it eliminates the solubility correction, but the use of the volatile ether is a disadvantage.

The methods in which chlorides are precipitated rather than extracted most closely approximate the usual analytical processes and are theoretically more accurate. However, Palkin's process is, strictly speaking, not really such, as the precipitant does not carry a component which enters into the composition of the precipitate formed; moreover, the method is applied to saturated rather than dilute solutions.

The object of the present paper is the development of a method for the separation and determination of lithium and sodium, based upon precipitation of the material separated, in a manner analogous to the usual analytical practice.

#### THE METHOD.

The process, in brief, consists in the precipitation and separation of sodium chloride from a solution of the mixed perchlorates of sodium and lithium in *n*-butyl alcohol by the addition of a butyl alcohol solution of hydrogen chloride according to the reaction,  $\text{NaClO}_4 + \text{HCl} = \text{NaCl} + \text{HClO}_4$ . The reagent is added to the solution of the perchlorates until a 6 per cent. acid concentration is attained. The precipitated sodium chloride is filtered on a weighed Gooch crucible, washed with a 6-7 per cent. solution of hydrogen chloride in butyl alcohol, dried at 250° and ignited for a few minutes at 600°. The lithium chloride, after removal of the organic matter by evaporation, is determined by conversion to lithium sulphate, a correction being applied for the almost negligible amount of sodium chloride remaining in the filtrate. In some cases the reagents give a slight blank. Potassium cannot be present since its perchlorate is insoluble in alcohol.

#### PREPARATION OF MATERIALS.

*Normal Butyl Alcohol.*—This material is readily obtainable on the market at the present time at a moderate price. The alcohol used in this research had a boiling range of 112-118° and a density of 0.8065 at 25°/4°; 60 per cent. of this product boiled within a range of 1° of the true boiling point. This fraction, when dried by reflux-

<sup>1</sup> The work done in connection with this paper was suggested by H. H. Willard and the preliminary work was carried out at the University of Michigan. The final work was done at the University of Illinois.

<sup>2</sup> Skinner and Collins, U.S. Dept. Agr., Bur. Chem. Bull., 1912, CLIII.

<sup>3</sup> Winkler, Z., anal. Chem., 1913, LII., 628.

<sup>4</sup> Palkin, Jour. Amer. Chem. Soc., 1916, XXXVIII., 2326.

ing with a slight excess of metallic calcium, periments were also carried out using alcohol had a boiling range of 116.2-116.7° and a density of 0.8060 at 25°/4°. Half of this fraction boiled within a range of 0.05°. In most of the work the 60 per cent. fraction, obtained as described above, was used. Ex-hol of widely different constants, the data concerning which will be recorded later.

*Perchloric Acid.*—The method of Willard<sup>5</sup> was used for the preparation of the perchloric acid. It was twice distilled under a pressure of from 5 to 15 mm. and contained about 72 per cent. HClO<sub>4</sub>. Ten g. of this material when evaporated in a platinum crucible gave an almost unweighable residue after ignition.

*Sodium Chloride.*—An imported product of highest purity was used.

*Sodium Perchlorate.*—This material was prepared by treatment of the purest sodium carbonate with a slight excess of dil. perchloric acid. The anhydrous sodium perchlorate was obtained by crystallisation above 50°, using centrifugal drainage. The product thus obtained was dried in a current of dry air at a temperature of 250°. To obtain samples of sodium perchlorate for the analytical separations, pure sodium chloride in weighed portions was evaporated on a hot plate with a slight excess of perchloric acid until fumes of perchloric acid were no longer evolved.

*Lithium Chloride.*—This material was prepared from a product which contained some sodium chloride. It was freed from the latter by solution in hot butyl alcohol under a reflux condenser. The solution was cooled and the sodium chloride filtered off. The lithium chloride in the filtrate was recovered by evaporation in a platinum dish to a partly mass which was dried in an electric oven at 100°. It was further heated in a muffle at 500°, and finally fused in a current of hydrogen chloride dried with sulphuric acid. The product thus obtained was cooled, crushed, and powdered under conditions which insured no contact with atmospheric moisture. It was used only in the solubility determinations.

*Lithium Perchlorate.*—The method employed in the preparation of this material was that described by Richards and Willard.<sup>6</sup> Lithium nitrate was purified by recrystallisation and then precipitated by the addition of hydrofluoric acid. The lithium fluoride was converted to perchlorate by evaporation with pure perchloric acid. This was then recrystallised from water with centrifugal drainage, platinum vessels being used throughout. The lithium perchlorate trihydrate thus obtained was dehydrated by fusion in a current of dry air at 250°.

Samples of this anhydrous lithium perchlorate were weighed into platinum crucibles contained in glass-stoppered weighing bottles and again fused by placing the crucibles in a drying tube at 250°, through which passed a current of dry air. The crucibles and contents were then replaced in their weighing bottles, cooled, and reweighed. The original weight was usually lowered a fraction of a milligram due to the very slight hygroscopic nature of anhydrous lithium perchlorate.

*The Solution of Hydrogen Chloride in Butyl Alcohol.*—Butyl alcohol was treated with hydrogen chloride generated in the usual way by the action of conc. sulphuric acid on sodium chloride or conc. hydrochloric acid; 200 cc. of 20 per cent. solution could be prepared in two or three hours. For testing the strength of these solutions an hydrometer serves admirably. For use in this connection a density-concentration curve was constructed between the limits of 0 and 20 per cent. hydrogen chloride.

#### CONDITIONS AFFECTING THE PRECIPITATION OF SODIUM CHLORIDE FROM A SOLUTION OF SODIUM PERCHLORATE IN BUTYL ALCOHOL.

Several factors, some unexpected, were found to influence the quantitative separation of sodium and lithium from solution in anhydrous butyl alcohol by the addition of the solution of hydrogen chloride in butyl alcohol.

(To be Continued.)

<sup>5</sup> Willard, *Jour. Amer. Chem. Soc.*, 1912, XXXIV., 1480.

<sup>6</sup> Richards and Willard, *Jour. Amer. Chem. Soc.*, 1910, XXXII., 4.

## CORRESPONDENCE.

## ISOTOPE OF COPPER.

To the Editors of THE CHEMICAL NEWS.

GENTLEMEN, — Readers of this Journal may remember that I made an attempt to prove that copper was composed of whole-number isotopes in such proportion as to give a mean value as the atomic weight of this element, viz., 63.57. The values suggested in this Journal of March 20, 1914, page 143, were 63 and 67.

W. D. Harkins, in *The Journal of the American Chemical Society* for June, 1923, on page 1429, predicts the values 63 and 65.

Now, A. J. Dempster, in *Nature* of July 7, 1923, records having obtained positive rays of copper by means of a molybdenum furnace heated with a coil composed of molybdenum wire embedded in alundum cement. Three isotopes were observed, having provisionally the values 62, 64, 66.

Should Dempster's values be confirmed by further experiments, it will show the utter futility of attempting *precise* predictions based upon rather meagre evidence, but the general result indicated as far back as 1914 will have been confirmed.—Yours, &c.,

F. H. LORING.

## NOTICES OF BOOKS.

*Atomic Structure and Spectral Lines*, by A. SOMMERFELD, Translated from the third German Edition (1922) by H. L. BROSE. Pp. XIII. + 626 and 125 Figures in text. London: Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C.2. 1923. 32s. net.

It is one thing to possess a book and another thing to understand all that is in it. Prof. Sommerfeld's book, now a classic, contains much that requires very special study to understand fully, but there is a great deal of information clearly presented, thanks to the translator; and all who are interested in the fundamental characteristics of the atom, as studied and investigated more particularly by the physicist, should add this volume to their library, and study it.

In order that the reader may form some idea in advance of the scope of this work, the following sub-headings have been selected out of a total number of about 100: Atomicity of electricity; ions and electrons;

photo-electric effect and its converse; glimpses of the quantum hypothesis; radio-activity; nuclear charge and atomic number; the atom as a planetary system; laws of radio-active displacement and the theory of isotopes; peripheral and central properties of the atom; visible and Röntgen spectra; configurations of the inert gases; Laue's discovery; survey of the K, L, and M series; corresponding limits of excitation; K series and its bearing on the periodic system; L and M series; doublet relationships; introduction to the quantum theory; empirical data about the spectra of hydrogen; principle of combination; Bohr's theory of the Balmer series; elliptic orbits in the case of hydrogen; quantising the spatial position of Kepler orbits; theory of the magneton; spherical wave and its propagation; conservation of energy and momentum; principle of selection and rule of polarisation; orbits of hydrogen in the Stark effect; Zeeman effect; quantum theory of the series scheme; principle of selection for the azimuthal quantum; testing the series scheme by the method of electronic impact; spectroscopic law of displacement and law of exchange; visible bands; meaning of the head of the band; law of the edge of the band; many lines spectra; preliminaries concerning the theory of relativity; variability of mass and inertia of energy; relativistic Kepler motion; fine structure and the relativity correction; doublets of the Röntgen spectra; spectroscopic confirmation of the theory of relativity, Bohr's principle of correspondence, &c.

Prof. Sommerfeld, as we all know, has developed a theory of the fine structure based upon Bohr's classical work in explanation of the spectra of hydrogen and helium, but the theory in some respects extends to all elements. In the "theory of the fine structures there is a confluence of the three main currents of modern research in theoretical physics, namely, the theory of electrons, the theory of quanta, and the theory of relativity. This is exhibited in a particularly vivid way in the way our *fine-structure constant*  $a$  is built up:— $a = 2\pi e^2/hc$ . Here  $e$  is the representative of the theory of electrons,  $h$  is the worthy representative of the quantum theory, and  $c$  comes from the theory of relativity and, indeed, characterises it in comparison with the classical theory."—Page 525.

From the foregoing it will be seen that in developing a theory of the atom based upon electron movements, much of modern phy-

sics has been brought into the problem, and on this account the book becomes a treatise of considerable scope.

Apart from the more rigorous treatment, there are ideas introduced in a suggestive way which will afford food for those in search of advance information. As an example, the question of two kinds of electricity is not made so evident by *current* electricity, which is a flow of electrons, for in terms of electrons the unity idea is prominent. In atomic physics, however, a positive charge signifies more than the absence of a negative charge, since "positive electricity is always associated with ordinary matter." The difference, therefore, implies "types of electricity that differ not only in sign but also in nature," which are individualised in the electron and the positively charged H atom. Quoting from page 22, "We can picture an atom (or a body) as highly charged negatively as we like, that is, we can add to it any number of negative electrons"; whereas, we can only increase the positive charge "to a certain maximum amount so long as we do not considerably alter the mass." We can remove from the atom only as many electrons as it possesses at the outset. According to the theory of relativity, no inherent or relative change in charge can take place. Electricity thus becomes a *substance*, but there are *two* such substances. "The charge and the mass are hereby indissolubly associated with one another, the negative charge with the electronic mass, the positive charge with the hydrogen mass."

In discussing *polarisation*, Prof. Sommerfeld states that "it signifies that a ray favours a certain plane passing through it more than the one perpendicular to this plane." The early idea that Röntgen rays were longitudinal vibrations involves the scheme of symmetry, and therefore polarisation becomes impossible, since Barkla discovered that *primary* Röntgen rays are partly polarised, and that *secondary* Röntgen rays are wholly polarised in certain directions. The longitudinal vibration theory thus breaks down, and we are left with the interpretation that the direction of vibration does not correspond with the direction of motion of matter, but that the vibration is that of electric force which "participates in the wave-radiation." In wireless telegraphy the emission is zero in the direction of the alternating current, corresponding to its component of acceleration, but at right

angles to the antenna the emission becomes a maximum.

The theory of *fine-structure*, which Prof. Sommerfeld has developed with great mathematical skill, follows when the Bohr theory of stationary states involving the quantum theory is analysed by means of relativity mechanics involving the change of mass of the electron with a change in its orbital velocity, so that those lines which were regarded as coincident become separated into a configuration of closely associated lines owing, as is evident, to the relativity effect involved. The velocity of the electron is less at the aphelion than at the perihelion, and this difference becomes greater as the eccentricity of the orbit increases. Quoting from page 475: "Thus the observation of the fine-structures discloses the whole mechanism of the intra-atomic motions as far as the motion of the perihelion of the elliptic orbits. The complex of facts contained in the fine-structures has just the same importance for the special theory of relativity, and for the atomic structure as the motion of Mercury's perihelion for the general theory of relativity." It is important to note that without the theory of relativity it would have been impossible to develop the theory of fine structure.

In a work of this magnitude errors are bound to occur in the first translated edition. These do not, however, detract from the value of the book. On p. 12, 5th line from top, *captivity* would be a better word than "capacity." Two lines further down, on the same page, the wording, "Although they here also soon," could be improved. On p. 23, the expression, "soup-plate," seems to imply a shape not strictly accurate, and it is not in dignified keeping with the subject.

On p. 84 it is stated that "*isotopic elements cannot be separated from one another by chemical means at all, and exhibit identical physical properties throughout.*" Atomic mass is a physical property and, in the case of some isotopes of a given element, it varies to the extent of eight units, as stated in the same paragraph. The above sentence is faulty in two respects; for (1), there are some physical properties which are not identical, and (2) the word *element* is more correctly used in a collective sense, and it should not be used synonymously with the word *atom* in this connection. An element is a collection of atoms of the same chemical kind with one common atomic number, except in the case of radio-active

elements which receive different names owing to their radio-active properties, or radio-active origins, differing.

On p. 101, 7th line from bottom, "inner" should read *outer*. On p. 102, 20th line from top, "elements" should read electrons. On the same page, and on p. 86, the practice of placing mass-numbers partly below the type line should be discouraged; they should be above it, or level with it, otherwise confusion with chemical notation arises. The meagre reference to Sir J. J. Thomson's pioneer work on the atom is a serious omission in a book of this scope. The general get-up and printing of the book leaves nothing to be desired. The up-to-date and complete X-ray-spectra tables in Chapter III. will be appreciated.

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*The Constitution of Matter*, by MAX BORN, translated by E. W. BLAIR, D.I.C., B.Sc., A.I.C., and T. S. WHEELER, B.Sc., A.R.C.S.I., A.I.C. Pp. VII. + 80, London: Methuen & Co., Ltd., 36, Essex St., W.C.2. 1923. Price 6s.

This volume is based upon three important essays which Prof. Born has amplified and published in book form. The importance of the subject matter may be inferred from the fact that a second edition was soon demanded, and upon it the present translation is based.

An outline is given of the knowledge of atomic structure gained during the last few years, especially as the result of much patient investigation in the field of Atomic Physics.

The methods of measuring the charge and mass of an electron and the various models of atomic structure are described, together with such matters as the X-ray diffraction by crystals, and recent work on X-ray spectra.

Reference is made to the general theoretical development of the subject by Sommerfeld and by Kossel.

Prof. Born further develops his outline of the constitution of matter from a study of the inter-atomic forces in solids.

There is no index, but an extensive bibliography is appended to each section.

It will be realised that little more than a critical examination of the results of physical investigations in Atomic Science is possible in Prof. Born's admirable survey of the subject, which does not pretend to be an exhaustive account of all the Atomic Theories.

The Department of Scientific and Industrial Research has issued a *Report of the Fuel Research Board for the Years 1922-23*.—*First Section: The Production of Air Dried Peat*. Pp. VII. + 146. Price 5s. 4d. post free.

The investigations made since 1919 by Prof. Purcell and his assistant, Mr. E. J. Duffy, B.Sc., on the production and utilisation of air-dried peat are contained in this valuable report.

In 1921, the report of the Irish Peat Inquiry Committee was published, together with recommendations and other documents showing why it was not found possible to carry out the large experimental scheme of peat winning recommended.

Peat, as found in undrained Irish bogs, contains as much as 92 to 95 per cent. of water. Draining reduces it to between 88 and 91 per cent.

Peat cannot be usefully employed as a fuel until the moisture content is below 30 per cent. No economic method of drying by artificially generated heat is yet available, and where peat is used commercially it has been air-dried. The report, therefore, deals only with air-dried peat.

Mr. Duffy has investigated the properties of air-dried peat and the factors which govern the rate of drying of both hand-cut and machine-formed blocks. His report is given in an appendix.

Professor Purcell visited Canada in 1920, to see the work the Canadian Peat Committee was carrying out for the Federal and Provincial Governments on the mechanical production of peat, and in 1921 and 1922 he visited Germany and Sweden for the purpose of studying the latest practices in these countries. His reports are also given in appendices.

The winning of peat on a small scale has been successfully practised from time immemorial, but the problem of large scale production is far more difficult.

Professor Purcell has dealt with these difficulties and has visualised possible schemes for peat winning on a scale of 100,000 tons per annum from one bog area over a period of years.

This report, which is very fully illustrated, may be had from H.M. Stationery Office, Imperial House, Kingsway, W.C.2, and also from the provincial and colonial offices and agencies.

*Alcoholic Fermentation*, by ARTHUR HARDEN, PH.D., D.Sc., F.R.S. Pp. 194. London: Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 1923. 6s. 6d. net.

The subject of alcoholic fermentation has been of interest and importance from the earliest times.

Periodically in the development of scientific knowledge some great advance has been made towards the elucidation of the true mechanism of the chemical changes involved in this process.

One of the earliest discoveries was that of van Helmont who, in the 17th century, distinguished the evolution of carbon dioxide (gas sylvestre) in the course of alcoholic fermentation.

The next real step forward was made almost simultaneously (1837) but independently by three observers, Cagniard-Latour, Theodor Schwann, and Kützing, who demonstrated that the yeast which performed the fermentation was a living organism. This paved the way for Pasteur's researches, which mark the next advance, since he conclusively showed that there could be no fermentation without life.

Finally there is Buchner's discovery (1897) of the enzyme, zymase. This authority showed that the action of the yeast is due to ferments secreted by the cells of the yeast plant.

It is now further known that zymase, which is essential for the fermentation of sugar, only does so in the presence of a second body, called for want of a better term, the co-enzyme. The nature of this mysterious co-adjutor is at present unknown.

It withstands heating to 100° C., and is also dialysable and may be simpler in constitution than zymase.

Another essential condition for the fermentation of sugar, as Prof. Harden himself has proved, is the presence of a phosphate. The way in which this substance enables the decomposition of the carbohydrate into carbon dioxide and alcohol (and other substances) to occur is very ably described.

Prof. Harden's monograph constitutes a most important contribution to Organic Chemistry, and the border subject of Biochemistry. J.G.F.D.

*Supplementary Notes on Gravimetric Analysis*, by W. Lowson, B.Sc., F.I.C. Pp. 54. London: Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 1923. 2s. 6d.

In this little volume the author has collected together those important points in manipulative work, which are seldom given in ordinary laboratory manuals.

It is just these essential hints that enable the average student to acquire skill and accuracy in conducting quantitative analyses.

This section of practical chemistry is apt to become tedious to some students, especially if through lack of supervision or help they unconsciously neglect some apparently trivial operation, or accidentally introduce an error into their work, thus feeling discouraged by poor results.

The book should therefore be of service to demonstrators. It includes, in spite of its title, a chapter on the calibration of volumetric apparatus, as well as others on some typical Estimations and Occlusion.

The introductory section on Apparatus and Manipulation contains much useful information for beginners.

#### BOOKS RECEIVED.

*A Treatise on Chemistry*, by The Right Honourable SIR H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Pp. XII. + 829. Vol. II., Part I. 1923. Messrs. Macmillan & Co., Ltd., St. Martin's St., W.C.2. 50s. net.

*A Treatise on Chemistry*, by The Right Honourable SIR H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Pp. VIII. + 1,563. Vol. II., Part II. 1923. Messrs. Macmillan & Co., Ltd., St. Martin's St., W.C.2. 50s. net.

*Organic Chemistry*, by IRA REMSEN, Revised and Enlarged by W. R. ORNDORFF, Ph.D. Pp. XI. + 567. 1923. Messrs. Macmillan & Co., Ltd., St. Martin's St., W.C.2. 10s. net.

*The Structure of the Atom*, by E. N. DA C. ANDRADE, D.Sc. (LOND.), Ph.D. (HEIDELBERG). Pp. XIV. + 314. 1923. Messrs. Bell & Sons, Ltd., York House, Portugal Street, W.C.2. 16s. net.

*Quantitative Chemical Analysis and Inorganic Preparations*, by R. M. CAVEN, D.Sc. (LOND.), F.I.C. Pp. VI. + 156. 1923. Messrs. Blackie & Sons, Ltd., 50, Old Bailey, E.C. 3s 6d. net.

*The Paper-Makers' Directory of All Nations*. Pp. XLIX. + 971. Thirty-second Edition. 1923. Messrs. Dean & Son, Ltd., Debrett House, 29, King Street, Covent Garden, W.C.2. 21s.

SYNTHESIS OF  $\alpha$ -DIKETONES BY  
MEANS OF ORGANO-ZINC  
DERIVATIVES.

By E. E. BLAISE.

The author has previously shown that the condensation of zinc propyl iodide with oxalylbisoxoisobutyryl chloride gave a mixture containing propyl-glyoxal and dibutyryl bis-cycloacetatoxyisobutyrylates. After alcoholysis of the mixed products the latter remains alone. This formed a crystalline substance, which melted at 55-80°, and was a mixture of the internally compensated and the racemic isomers. These were only separated by slow crystallisation from methyl alcohol, followed by mechanical separation of the two kinds of crystals isolated. The pure substances melted at 72° and 82° respectively, and boiled at 168° C. under a pressure of 13 mm. The hydrolysis of the mixed isomers by means of hydriodic acid was accompanied by reduction, and propyl *n*-butyl ketone was formed, which boiled at 163° and gave a semicarbazone. This melted at 96° C. Hydrolysis by means of a mixture of hydrochloric and acetic acids gave a 60 per cent. yield of dibutyryl. It is a yellow liquid, b.p. 61.5° C. under a pressure of 14 mm. The dioxime melted at 181-182°, and the disemicarbazone not below 250°.

(From *Compt. rend.*, 1923, CLXXVI., 1148-1150.)



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Latest Patent Applications.*

16138—Coley, H. E.—Reduction of sulphides. June 21.

*Specifications Published this Week.*

198705—Plauson, Dr. H.—Process and apparatus for the recovery of oils, bituminous matter, tar and resin from bituminous shale, oil-bearing sands, bleaching-earths, peat, brown coal, coal and wood.

198825—Chemische Fabriken vorm. Weiler-ter-Meer.—Process for impregnating wood.

198829—Soc. of Chemical Industry in Basle.—Manufacture of a new derivative of pyrazolone and of new dyestuffs therefrom.

198855—Royal Baking Powder Co.—Apparatus for effecting chemical reactions by means of amalgams.

198975—Vains, A. R. De.—Processes for dissolving the organic products obtained by the chlorination of cellulose material.

*Abstract Published this Week.*

197223—Sodium chromate.—Baumgartner, E., of 6, Kamstrupsti, Roskilde, Denmark.

*Sodium chromate* is obtained by heating in a current of hot air in a muffle, a mixture of chromium ore with sodium carbonate with or without lime or calcium carbonate. The materials are formed into briquettes and are arranged in the muffle, for instance, in rows with spaces between so as to allow contact with the current of air. Stirring or turning of the charge is unnecessary and undesirable and the operation is complete in one burning.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each,



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3302.

## BRIDGING THE GAP IN THE SPECTRUM.\*

Hertz's classical experiments with electric waves in 1888 not only paved the way for the development of wireless communication, but showed that these waves, as indicated by Maxwell's electromagnetic theory of light, were waves of the same kind as light, for they could be bent by prisms and shown to be a part of a spectrum. The electric waves which Hertz produced in his laboratory were 60 cms. long.

It was not until 1895 that Lebedew obtained electric waves which had a length of 6 mms. Lampa, about the same time, had produced waves of 4 mms. in length. Möbius, in 1918, confirmed the general results of the two foregoing investigators, but he came to the conclusion that their waves were respectively 10 and 7 mms. long. Möbius, from experimental considerations, deduced evidence that in this case anything shorter than the above were ripples as distinct from regular waves.

At this time, following Langley's researches on the solar spectrum, Rubens and Paschen investigated the infra-red end of the spectrum and detected waves  $9.4\mu$ , which is 16 times longer than the wave-length of yellow light.

In 1897 Rubens and Nichols, by means of a multiple-reflection method, succeeded in extending the boundaries of the infra-red spectrum ten-fold. Then the former investigator obtained a further extension by employing Wood's method of focal isolation. Following on this, Rubens and von Bayer, in 1911, measured infra-red waves up to 0.320 mm. in length.

There remained a gap between the heat waves and those produced by electrical apparatus, but this gap Nichols and Tear have now bridged by electrical waves, using a method which is briefly described in the *Proceedings of the National Academy of Sciences of U.S.A.*, Vol. IX., No. 6, June,

*Rev.*, 1896-7, Vol. IV., p. 297), which received the waves. The usual blackened vanes in this radiometer were replaced by mica strips, on which were deposited bright metallic platinum. By shielding the vanes on one side, their rotation was obtained, as the action of the electric waves produced oscillating currents in the metal, which perceptibly heated it owing to its ohmic resistance, and thus gave rise to the well-known radiometer action. The short electric waves were generated by means of a Hertzian doublet with minute tungsten cylinders substituted for platinum. The wave-length measurements involved the use of a new form of reflecting echelon analyser.

By means of the equipment briefly sketched above, Nichols and Tear were able to produce and measure electric waves down to 0.220 mm. in length, which is "shorter than the longest known heat waves emitted by matter at high temperatures." In a check experiment on the apparatus, these investigators exposed their electric-wave receiver to Rubens' and von Bayer's heat waves of 0.320 mm. in wave-length, and obtained "results identical with those recorded by these earlier investigators."

The range represented by the shortest wave-length, that of gamma rays ( $\gamma$  rays) from radio-active matter, to that of the longest Hertz waves, is now practically explored throughout. The ratio of the shortest wave-length to the longest wave-length is about 1 to 20 million billion.

"Matter under the action of heat is capable of giving off radiations in the so-called infra-red, visible, and ultra-violet spectra; gamma rays are the natural accompaniment of radio-active disintegration, and there are various electric phenomena in the atmosphere giving rise to pulse-like disturbances resembling fragments of very long electric waves. But X-rays and the old and new short electric waves we may still regard as artificial, or purely products of laboratory manufacture."

### THE INSTITUTE OF PHYSICS.

At the last meeting of the Board the following Corporate Members were elected:—  
 Fellows: C. H. Desch, M. Fishenden, W. M. Jones, S. Marsh; Associates: R. P. Black, M. Brotherton, J. F. Congdon, D. E. Jolin, H. Lowery, S. P. Peters, L. J. Sutton, N. W. Turnell, A. Whitaker, L. Wright.

\* Compiled from Nichols and Tear's paper in the "Proceedings of the National Academy of Sciences of U.S.A.," Vol. IX., No. 6, June, 1923.

### THE BRITISH DYE INDUSTRY.

During a recent debate on the Board of Trade vote in the House of Commons, Mr. Clayton, the Unionist member for Widnes, referring to British dyes, said that we had all the raw materials for the dye industry in this country, and there was no reason why those dyes which were made before the war in Germany could not be made here. Enormous progress had already been made, and the dye-users agreed that under the help and guidance of the present Board of Trade they would yet establish a dye industry in this country which could hold its own with any other. The intermediates for these dyes were necessary for explosives, and if the dye industry was maintained in this country we should have valuable materials at our disposal in case of emergency. Before the war in Germany it was part of the Army manœuvres to turn the dye-works into explosive factories. He maintained that the chief opposition to this subsidy came from the merchants who supplied German dyes.

Sir P. Lloyd-Greame, President of the Board of Trade, said that the value of the dye industry to the textile industry of this country was greater than ever before. The occupation of the Ruhr had taken place, and great uncertainty existed as to whether the dyes would come forward at all. He knew one company which had been manufacturing day and night almost since the occupation to supply the things that were needed. The textile trade would have been in a very anxious position in the last six months if it had existed entirely on dyes coming from the Continent. It had been said that the dyes that were being used in Lancashire were bad, but the Chairman of the Dye-Users' Association had paid a tribute of admiration to the makers for the progress achieved in the production of dyestuffs in the last few years. Our pre-war consumption of German and other foreign colours was 70 to 80 per cent. of the total, and last year we used 70 to 80 per cent. of British dyes, this change having been effected without in any way reducing our standards.

### STUDIES ON THE PHYSICAL FOUNDATIONS OF DEEP THERAPY TREATMENT.

BY PROF. DR. FRIEDRICH DESSAUER

(Director of the Institution for the Study of Physical Laws of Medicine, University of Frankfurt, Frankfurt-on-the-Main, Germany.)

#### STUDY OF THE PHYSICAL CONDITIONS.

The paper dealt first with the physical laws of irradiation and the exact knowledge of the distribution of the rays within the tissues.

The second line of study covered the technical requirements for a practical solution of the problem. I have been working in Germany on the development of the apparatus, and have spent many years of thought on producing one that would generate very high voltages and would operate continuously without change under conditions of absolute safety and within small dimensions; that is, an apparatus which could be used by the medical man without danger and without great expense for operation and upkeep. In the meantime my friend and co-worker, Dr. W. D. Coolidge, has still further developed his wonderful tube, with which I could obtain the

most accurate results, and with which I could bring to their best effect the high voltages. This subject will be covered in my second paper.

Before arriving at my last results, I shall briefly touch upon the history of how the problem started. In 1904, nearly seventeen years ago, I first formulated the problems. At that time superficial skin diseases were being treated with Röntgen rays. The results were not satisfactory, and Professor Perthes published interesting experiments, coming to the conclusion that an insufficient quantity of rays penetrate to a depth. I naturally approached the problem from the physicist's point of view.

The *Laws of Homogeneous Irradiation* were the foundation for the development of deep therapy, and have to-day proven to be true. To-day it is very simple and natural, but it was not so seventeen years ago, when the nature of Röntgen rays was unknown and their laws could not have been known. Amongst those who had grasped at the first the importance of the physical laws of deep therapy and had made use of them consciously, I should like to mention Beclère of Paris and Wetterer of Mannheim.

The laws of homogeneous irradiation are in abbreviated form the following:

*First Law.*—The foundation of Röntgen-otherapy is formed by the biological ex-

perience that different cell forms show different sensitiveness to the same Röntgen rays.

*Second Law.*—Rays of different penetration are to be regarded as different medicaments, so long as the contrary is not proven. The difference in sensitiveness of different cells appears more marked if hard rays are applied.

*Third Law.*—In order to determine and utilise precise differences in sensibility, the homogeneity of the field of radiation is a required condition.

*Fourth Law.*—The non-homogeneity of a treated field detracts from the effect. The conditions for a favourable influence upon the disease are not fulfilled when the non-homogeneity of the field is greater than the difference in sensitiveness between the diseased cells and the healthy.

This law, the law of the *limit of effect*, can easily be expressed by algebraic formulae.

*Fifth Law.*—There is a homogeneity of space or quantitative homogeneity and a specific homogeneity, or qualitative homogeneity. The aim must be to dose the diseased zone throughout its extent with the needed quality or dose of irradiation, and to have this dose of the same quality throughout.

*Sixth Law.*—The condition of qualitative or specific homogeneity is fulfilled when the irradiation in the complete zone during its course through the body does not change its composition or consistency. The reaction on the different cells is then physically only dependent on the *intensity and the time*.

*Seventh Law.*—The intensity of effect may not differ more than the degree of sensitiveness. This is only a more precise statement of the fourth law, the *limit of effect*, but one may try to increase the intensity on the diseased zone in the depth and to raise it above the intensity on the surface, and in the vicinity of diseased cells.

Having a *well-known composition of rays we have measured the distribution of the intensity of irradiation within a body*. These measurements have been made with four kinds of rays—the most penetrating which up to then could have been produced continuously. Five focal distances were studied each for three different-sized treatment fields—small, medium, and large.

(From "*The American Journal of Roentgenology*," Vol. VIII., No. 10, October, 1921, pages 578-588.)

#### AGRICULTURAL MACHINERY EXHIBITION AT PARIS.

The Department of Overseas Trade is in receipt of information that the Third Agricultural Machinery Exhibition will be held in Paris in January, 1924.

This exhibition, like those held in 1922 and 1923, will include agricultural machines and implements manufactured in France or in countries which were allied, associate or neutral during the war.

Applications for space will be received up to October 15 next, by the Commissariat General, 8 rue Jean Goujon, Paris (8e).—(From the "*Board of Trade Journal*," July 12, 1923.)

#### INTERNATIONAL SAMPLES FAIR AT ZAGREB.

The Department of Overseas Trade is informed that the Third International Samples Fair is to be held at Zagreb (Agram), Jugo-Slavia, from April 27 to May 5, 1924.—(From the "*Board of Trade Journal*," July 12, 1923.)

#### CANADA.

##### SURGICAL INSTRUMENTS AND HOSPITAL SUPPLIES FOR VANCOUVER, B.C.

H.M. Trade Commissioner at Vancouver reports that a firm in that city is desirous of receiving from United Kingdom firms, catalogues, prices, etc., relative to surgical instruments and hospital supplies. Further particulars can be obtained on application to the Department of Overseas Trade (Room 53), 35, Old Queen Street, London, S.W.1.

##### RAPESEED OIL REQUIRED IN U.S.

Mr. G. Campbell, H.M. Consul-General at San Francisco, reports that a local firm of import and export merchants are desirous of receiving c.i.f. quotations for linseed and refined deodorised rapeseed oil. In the case of the former, the company wish to deal with London exporters alone, and in the case of the latter only with manufacturers.

British firms desirous of receiving further particulars of this enquiry should apply to the same Department. (Reference 20066/F.W./C.C.2.)

OBSERVATIONS UPON AND  
DEDUCTIONS FROM THE FIGURES  
GIVEN IN THE INTERNATIONAL  
TABLE OF ISOTOPES, 1923.

By HAWKSWORTH COLLINS.

In this paper it is inferred that all the figures given in the International Table of Isotopes, 1923 (which appeared in *The Chemical News*, 1923, CXXVI., 147), are results obtained by independent experi-

ments, and that no one of them is merely the result of hypothesis; *e.g.*, 18 has been obtained by independent experiment as the atomic number of Argon. If it has not been so obtained, it would not have appeared in the table, for the duty of the new Committee is "to keep chemists informed of the various advances made each year in this field," and the word "advances" evidently does not include anything of the nature of hypothesis.

TABLE I.

Element	Atomic Dominant			Atomic Number	Remark	Maximum	
	Weight	Isotope	Remark			Valency	Remark
He	4.00	4	even	2	even	2	even
Li	6.94	7	odd	3	odd	1	odd
Gl	9.1	9	odd	4	even	3	odd
B	10.9	11	odd	5	odd	3	odd
C	12.005	12	even	6	even	4	even
N	14.008	14	even	7	odd	5	odd
O	16.000	16	even	8	even	2	even
F	19.0	19	odd	9	odd	1	odd
Ne	20.2	20	even	10	even	0	even
Na	23.00	23	odd	11	odd	1	odd
Mg	24.32	24	even	12	even	2	even
Al	27.0	27	odd	13	odd	3	odd
Si	28.1	28	even	14	even	4	even
P	31.04	31	odd	15	odd	5	odd
S	32.06	32	even	16	even	6	even
Cl	35.46	35	odd	17	odd	7	odd
A	39.9	40	even	18	even	0	even
K	39.10	39	odd	19	odd	1	odd
Ca	40.07	40	even	20	even	2	even
Fe	55.84	56	even	26	even	6	even
Ni	58.68	58	even	28	even	3	odd
As	74.96	75	odd	33	odd	5	odd
Br	79.92	79	odd	35	odd	7	odd
Rb	85.45	85	odd	37	odd	3	odd
I	126.92	127	odd	53	odd	7	odd
Cs	132.81	133	odd	55	odd	5	odd

OBSERVATION 1.

When the atomic number is even, the masses of the isotopes are even whole numbers; and when the atomic number is odd, the masses of the isotopes are odd whole numbers; with a few exceptions.

There are 70 numbers given for the masses of the isotopes (not including the doubtful ones in brackets, and excluding also the mass of hydrogen which is not given as a whole number), and of these, 12 are exceptions to the above general rule. If we wish to know whether this general rule contains a truth, we must proceed in the following manner:—

The probability that, when the atomic

number is even, the mass of the isotope would accidentally also be even is 1 : 2, and that when the atomic number is odd, the isotope would also be odd, is 1 : 2. Therefore the probability that the above regularity would happen accidentally in 58 cases out of 70 is  $1 : 2^{70} - 2 + 12 = 1 : 2^{46} = 1 : 70$  billion.

So, the probability that this state of affairs has not happened by accident is 70 billion to one, that is, it is absolutely certain that a truth is contained therein.

*Deduction 1.*—Therefore, with the advance of knowledge, the exceptions will probably diminish; *e.g.*, the single odd iso-

tope of Se may be found later to be an impurity and not Se at all.

*Deduction 2.*—There is some fundamental and uniform connection between the atomic number of an element and its isotopic masses, and this connection must be expressible by whole numbers.

In the case of Li, whose atomic weight is given as 6.94, and whose isotopes are 7 and 6, it is evident that the majority of the isotopes must have masses of 7. A similar remark can be made in the cases of several other elements. Omitting those to which such a remark cannot be applied, the figures for dominant isotopes (given in Table I.) are obtained.

#### OBSERVATION 2.

When the atomic number is even (or odd) the dominant isotope is correspondingly even (or odd) in 24 cases out of 26.

The probability that this contains a truth is  $2^{26} - 2^2 \times 3^3 : 1 =$  four million to one.

*Deduction 3.*—There is some fundamental and uniform connection between the atomic number of an element and the mass of its dominant isotope, and this connection must be expressible by whole numbers.

The maximum valences given in Table I. are universally recognised as such.

#### OBSERVATION 3.

When the atomic number is even (or odd), both the dominant isotope and also the maximum valency are correspondingly even (or odd) in 23 cases out of 26.

The probability that this contains a truth is  $4^{26} - \frac{3 \times 4}{3} : 1 =$  17 billion to one.

This can be seen to be correct by the following consideration. If it were merely a matter of accident, only one out of every four elements would be likely to have 3 evens or 3 odds. Therefore, in 26 elements, 6.5 ( $=26/4$ ) would be likely to satisfy this condition; so that there would be 19.5 exceptions. (The fact that 19.5 is not a whole number does not affect the reasoning, of course). The probability would then be  $4^{26} - \frac{19 \times 5 \times 4}{3} : 1 = 4^0 : 1 = 1 : 1$ , which is evidently correct.

*Deduction 4.*—There is some fundamental and uniform connection between the atomic number of an element, the mass of its dominant isotope, and its maximum valency, and this connection must be expressible by whole numbers.

The following observation applies exactly to all but three of the first 19 elements in Table I., i.e., to the great majority of the common elements.

#### OBSERVATION 4.

The atomic number gives the number of 3's and 1's into which the mass of the dominant isotope can be split up, always commencing with a 3, and taking the 3's and 1's alternately.

*E.g.*, the atomic number of B is 5, and its dominant isotope can be split up into 5 parts, 3+1+3+1+3; the atomic number of Mg is 12, and its dominant isotope can be split up into 6(3+1), i.e., into 12 parts.

This state of affairs continues as far as Ca, when there is an abrupt change, and occurs no more at all in the elements of atomic weight greater than 40.

The probability that there is a truth involved in this observation is infinitely greater than  $2^{19} - 2^3 \times 3^3 : 1 = 8000 : 1$ , because it is a complex regularity.

#### OBSERVATION 5.

If the mass of the dominant isotope is an even number, the atomic number is obtained by halving it. And, if the mass of the dominant isotope is odd, the atomic number is obtained by subtracting one and then halving the result.

This state of affairs continues again as far as Ca, when there is an abrupt change, and occurs no more at all in the elements of atomic weight greater than 40.

The probability that there is a truth contained in this observation is  $2^{19} - 2^2 \times 3^1 : 1 = 130,000 : 1$ , for there is only one exception, viz., Argon.

*Deduction 5.*—It follows from the last two observations that the majority of the common elements of atomic weight less than 41 are differentiated absolutely from all other elements by some fundamental property or properties. Either this is the case, or the atomic numbers from Fe upwards are wrong. But since chemists are convinced that the properties of all elements are periodic functions of their atomic weights, they cannot admit that there is any fundamental regularity which belongs solely to those elements which happen to have atomic weights less than 41. Therefore the atomic numbers from Fe upwards must be wrong.

It is not merely extraordinary, but it is also quite absurd, that a complex general rule connecting the atomic weight with the atomic number should apply only to those elements which happen to have atomic weight less than 41, and which also happen to include nearly all the common elements.

*Deduction 6.* — The fourth observation evidently contains the fundamental and uniform connection, which has been proved to exist between the atomic number of an element and its dominant isotope, for there is no other uniform arrangement of whole numbers possible; and this is especially suitable, since it is known that one electro-positive force emanates from a mass of 1(1.008), also one from a mass of 3(H<sub>3</sub>), also two from 4(He).

## OBSERVATION 6.

If helium, with its two electro-positive forces, could be given off from the heptad Cl (35), a pentad would be left with atomic weight 31. The pentad P has at. wt. 31.

If helium were given off from the pentad P, there would be left a triad with at. wt. 27. The triad Al has at. wt. 27.

If helium were given off from the triad Al, a monad would remain of mass 23. The monad Na has at. wt. 23.

If helium were given off from the hexad S (32), there would be left a tetrad of mass 28. The dominant isotope of the tetrad Si has mass 28.

If helium were given off from the tetrad Si (28), a dyad of mass 24 would remain. The dominant isotope of the dyad Mg has mass 24.

If helium were given off from the dominant isotope (11) of B, a monad of mass 7 would be left. The dominant isotope of the monad Li has mass 7.

## OBSERVATION 7.

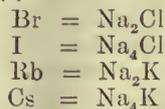
In all the above six examples, which are exact, the element which is supposed to be disintegrated has 2, 4, or 6 electro-positive valences, which always act in pairs, and which cause these elements to be classed as non-metallic.

The discovery involved in the last two observations was first published in an advertisement in *Nature* on June 14, 1906, long before chemists admitted that the atomic weights were whole numbers, or that the elements could be disintegrated, also several years before it was known that helium possessed two electro-positive valences. This new chemical law was worded as follows: "The non-metallic nature of an element is always due to a pair or pairs of electro-positive forces, each pair emanating from a portion of the element of which the mass is 4, taking the mass of an atom of hydrogen as unity."

If any chemist were asked to name three elements which are especially similar to one another, considering only the 33 given in the International Table of Isotopes, there is not much doubt that he would choose either Cl, Br and I, or K, Rb and Cs. It was shown in *The Chemical News*, Jan. 16, 1914, and Oct. 1, 1920, that Na (23) takes a prominent part in the formation of all elements of greater atomic weight than itself. This was done at a time when chemists objected to the mathematical proof that the atomic weights were whole numbers; but now that this difficulty has been almost entirely removed, the demonstration of the matter is much simplified.

## OBSERVATION 8.

Element	Isotopes	Observation
Cl	35	
Br	81	81 = 2 × 23 + 35
I	127	127 = 4 × 23 + 35
K	39; 41	
Rb	85; 87	85 = 2 × 23 + 39 87 = 2 × 23 + 41
Cs	133	133 = 4 × 23 + 41

*Deduction 7* :—

All these observations are matters of fact. There is no hypothesis, speculation, or guesswork involved in them. Also there is no arbitrary choice of facts; for all available data are employed, whether favourable or unfavourable.

There can be no valid objection to exceptions to general rules with respect to the structure of the elements, for there is no reason why all elements should be built up in exactly the same manner.

When a state of affairs has been proved to be due to cause and not to chance, it is evident that no future discoveries or additions to knowledge (such as isotopes, *e.g.*) can ever contradict the general truth obtained, for it is impossible for scientists to unconsciously evolve a state of affairs which can be proved to be due to cause and not to chance, and yet for it not to contain an absolutely incontrovertible truth.

The explanation of the odd and even observations evidently is: that if an even number of 3's and 1's be added together the result is even, and if an odd number of

3's and 1's be added together the result is odd.

From the above and additional observations, other deductions leading to the definite demonstration of the Constitution and Structure of the Elements were given in papers published in *The Chemical News*, Dec. 19 and 26, 1919, April 9, June 4, Oct. 1 and 15, 1920, etc.

#### THE ANNUAL MEETING OF THE ASSOCIATION OF BRITISH CHEMICAL MANUFACTURERS.

The Seventh Annual General Meeting of the Association was held at the Chemical Society's rooms on July 12. Sir Max Muspratt, Bart., Chairman of the Association, presided.

In proposing "That the report and accounts of the Association be and they are hereby adopted," the Chairman said the Association's sphere of usefulness is constantly increasing.

In spite of being chemical manufacturers, we have in recent years somewhat overcome the modesty of previous eras of chemical industry, and we believe that we have a message of a two-fold nature to give to the nation. We have a duty to perform in instructing Ministers and other members of the Government and the Civil Service as to what they ought to know about this most important industry. We have also to impress upon the nation at large that in Great Britain the chemical industry is a very important national asset, and, like every other important national asset, it has to go forward or go back. We intend, by every means in our power, to further the progress of this industry.

The British Industries Fair of 1923 is dealt with in the report, but I might accentuate the fact that in the British Industries Fair, both this year and on previous occasions, we have tried to carry out the policy of showing the close interlocking of the various branches of the chemical industry, and I believe at the recent British Industries Fair we carried that out to no small extent. The British Industries Fair is, we hope, an annual factor, but next year when the British Empire Exhibition also takes place, we felt that it would be calling too much upon our members to make an adequate chemical section on both those occa-

sions, and so we are not taking part in the Fair of next year. In the British Empire Exhibition of 1924 we are taking a very great part. We intend the Chemical Section of the British Empire Exhibition to be a complete survey of Britain's services to chemistry, from the smallest chemical manufacturer to the most brilliant and epoch-making discovery by scientific men in chemistry. It will be one of the most complete exhibitions of chemistry in its broadest sense that has ever been brought before the British public—greater than has been presented anywhere before. When I tell you that the Royal Society is going to take part in an exhibition, I think you will admit that we are bringing even the academic section of chemistry into the services of mankind and the Empire. The Chemical Society is, of course, assisting us; the Society of Chemical Industry; the Society of Petroleum Technologists; the Pharmaceutical Society; the Society of Dyers and Colourists are all assisting, and, from the Royal Society, Sir Herbert Jackson is *liaison* officer in conjunction with our General Manager, to see that the most complete linking up in absolute harmony of every aspect of chemistry is duly and properly carried out at the British Empire Exhibition next year.

With regard to the Continental situation, I believe that a few words will be said about that in another place to-day, and by one (the Prime Minister), who was a guest at our dinner last year. I need only deal with it purely from the aspect of chemical industry. The whole position of the Ruhr is one which the chemical industry, especially the fine chemicals and the dyestuff branches of the industry, has to look upon with great apprehension. There are superficial advantages in having competitors closed, but I am sure that nobody with the broad training of a chemist will for a moment take that aspect. On the purely material side, it is even better to have the chemicals in the hands of a competitive manufacturer than to have them in the hands of an irresponsible Government Department, and when that irresponsible Government Department is not even in this country, I need hardly say that what is going to happen to those dyes and other chemicals which have been taken by the French Government is causing grave doubt and grave uneasiness in the minds of everyone connected with the

Council of the Association of British Chemical Manufacturers.

I will not elaborate the paragraph in which the Dyestuffs Act is dealt with except to refer to the agitation for the repeal of that Act, and to ask if the real trouble of the textile industry is not the high price of cotton. I know I am speaking for everyone occupied with the heavy chemical industry in assuring him and his colleagues in other branches of the dye industry that the heavy chemical industry does desire to assist and co-operate with them in every possible way.

Turning to the question of alcohol, which has been discussed for years, and especially for months past, I should like to say how deeply we are indebted to Mr. Carr for the way in which he has handled this problem in conjunction with the Committee. It would be absolutely invidious to mention names, but I know that everyone of you will wish to add in your vote on this written report a vote of appreciation to the able staff who manage our affairs.

Mr. R. G. Perry, C.B.E., in the absence, owing to illness, of the Vice-Chairman, Sir William Pearce, seconded the resolution. He said there was only one point to which he would like to refer. It was the paragraph in the report which read: "The Council records with satisfaction and appreciation the honour which has been conferred by His Majesty the King upon its Chairman, Sir Max Muspratt, Bart." They all wished to congratulate their Chairman upon that honour. They were all quite sure that never had an honour fallen upon more worthy shoulders, and never would an honour be more worthily borne.

The Treasurer (Mr. C. A. Hill), in commenting on the accounts, said that, in case it should be thought they were working on too narrow a margin, he would like to put forward the view that that was a matter for congratulation to the administrative staff who were responsible for the working of the Association.

Mr. A. T. Smith said there was one matter of which they should make a special note, and that was the remarkable result which has followed their efforts as an association to better the chemical trade. They had one very particular instance to record, and it arose from the speech by Sir William Alexander, as Chairman of the British Dyestuffs Corporation. He (Mr. Smith) did not pretend that the results were due to the

efforts of the Association, but he did say that the fact that the Association lived and existed and did co-operate and help in every possible way, must have been of the utmost assistance to Sir William Alexander in the very arduous work he had undertaken. He might be perfectly certain, as far as the heavy chemical industry was concerned, that he would have the same co-operation in the future as he has had in the past, and he hoped the results would be quite as good.

Dr. E. F. Armstrong, F.R.S., said that the Association had certainly done well during the year, but it was desirable that chemical industry should try to stand on its own feet. He did not mean to criticise the policy of the Association in the past. Sir William Alexander, in the few words which he addressed to the shareholders of the British Dyestuffs Corporation, mentioned that a sum of £400,000 had been spent on research. The fact that it has been spent showed that one firm in this country realised the enormous importance of making itself strong on the scientific side as a preliminary to its success financially. It was only by research and by its technical work that they could get an advantage in the future. Whatever the Association did as its primary object, in the representation of the chemical industry as a whole, the Government must never lose sight of its secondary object, namely, the encouragement, first to co-operation, because that is the secret to other things, as Mr. Smith had indicated; and secondly, the encouragement of technical progress within their industry.

Sir William Alexander, K.B.E., C.B., C.M.G., D.S.O., said his company had received from the large members of the heavy chemical industry in recent times very real and concrete assistance in bringing down the prices of their products. In every case where it had been at all possible for them to meet the company they had done so, and in every case where it has been possible for the company to pay a higher price, they had paid it. He felt certain that their industry was going to pull through. He hoped that their industry would be of assistance to the other large industries which were embraced in the Association of British Chemical Manufacturers, and that as time went on they would find that they merited the confidence which was being placed in them.



The Rt. Hon. J. W. Wilson alluded to the last two paragraphs in the report with regard to transport.

Mr. F. H. Carr, C.B.E., F.I.C., referred to the alcohol question. The importance of alcohol to the fine chemical industry had perhaps never been stated, and yet he thought that chemical manufacturers and fine chemical manufacturers in particular were coming to realise that it was a substance, as a chemical, which they could use, whereas hitherto it has always been regarded as a substance which was beyond their reach. Many still believed that the chief use of alcohol was as a beverage. Chemists and Americans did not believe that. It was the raw material, the coal tar, of the pharmaceutical chemical. The ethyl group entered into a large proportion of the synthetic compounds used in medicine, and hitherto the manufacture of such compounds had been practically impossible owing to the difficulties which had been met with in the early stages of manufacture in getting satisfactory arrangements with the Excise Authorities. The work that had been done by the Committee had only been possible because of an entirely new state of affairs at the Board of Customs and Excise, and it was to such people as Sir Horace Hamilton and Sir Robert Robertson that their thanks must be chiefly given. They had in the concessions which they had given shown that we are at the dawn of a new era as regards the use of alcohol in chemical manufacture. The concessions which had been made permitted manufacturers who are commencing to use alcohol to use quantities up to 100 gallons without any restrictions as regards their receivers without the necessity of an officer being on the spot; and provided adequate figures were shown as regards the destination of the alcohol that was being used, they were quite satisfied to leave it with fairly moderate restrictions. He urged all those interested in fine chemical manufacture to make use of these privileges and to lay before the Association such difficulties as they might meet with in order that the Committee might go on with this work until they got every possible facility required for their manufacture.

Mr. Kenneth Chance, M.A., associated himself with the remarks of Mr. Wilson as to the question of transport.

Mr. E. V. Evans, O.B.E., F.I.C., expressed on behalf of the Society of Chemi-

cal Industry its appreciation of the help and contributions made by the Association to its Journal.

Dr. H. Levinstein, M.Sc., referred to a sentence in the report stating: "The Council has been asked, and has agreed, to organise the Chemical Section of the Exhibition to be held at Wembley next year." That was a remarkable testimony to the Association. The mere fact that when they had a British Empire Exhibition the whole of the chemical exhibit could be dealt with by one organisation of this kind showed what an enormous stride the chemical industry had made in organisation since the last exhibition of the same kind was held. He had not the slightest doubt that this chemical exhibit would make the same impression on chemists visiting the British Empire Exhibition as the wonderful exhibit shown by the Germans in Paris in the year 1900, which no doubt many of them remembered.

Mr. Bernard Hickson endorsed the remarks with regard to transport.

Mr. T. D. Morson said that as a backbencher he hoped that publicity would remain in the fore-front of the policy of the Association.

The Chairman, having briefly replied, then put the motion to the meeting, and declared the report and accounts unanimously adopted.

The Ordinary Meeting was followed by a Special General Meeting, when the amount of the annual subscription payable by members of the Association for the year 1923-1924 was fixed at four-fifths of the sums laid down in Article 17 of the Articles of Association.

Sir John Brunner, Bart., proposed, and Mr. R. G. Perry, O.B.E., seconded, a vote of thanks to the Chairman, which was carried unanimously, and the proceedings then terminated.

#### THE SEPARATION AND DETERMINATION OF SODIUM AND LITHIUM BY PRECIPITATION FROM ALCOHOLIC PERCHLORATE SOLUTION.<sup>1</sup>

By H. H. WILLARD and G. FREDERICK SMITH.

[Contribution from the Chemical Laboratories of the University of Michigan and the University of Illinois.]

(Continued from Page 43.)

It was found to be sufficiently close to a straight line function so that values be-

tween those given in the following table could be obtained by interpolation.

TABLE I.

*Density of Solutions of Hydrogen Chloride in Dry Normal Butyl Alcohol.*

HCl %	Density	HCl %	Density
0	0.8060	11	0.8685
1	0.8130	12	0.8930
2	0.8195	13	0.8770
3	0.8255	14	0.8810
4	0.8315	15	0.8855
5	0.8370	16	0.8895
6	0.8425	17	0.8935
7	0.8485	18	0.8960
8	0.8540	19	0.9010
9	0.8590	20	0.9050
10	0.8635		

These values were obtained by using a pycnometer and thermostat and refer to 25°/4° corrected to vacuum. The hydrochloric acid was determined by titration with standard alkali.

The factors in the order of their importance are: (1) temperature of precipitation; (2) concentration of hydrochloric acid, giving minimum solubility of sodium chloride; (3) conditions favouring ease of filtration; (4) prerequisites or drying and ignition of the sodium chloride obtained; (5) physical constants of butyl alcohol used in the method; (6) treatment of filtrates from sodium chloride for recovery of lithium. These factors will be taken up in the order given.

*Temperature of Precipitation.*—Sodium chloride precipitated from boiling solutions of sodium perchlorate in butyl alcohol when filtered on asbestos, washed, and dried at 250° for a long time, is perfectly white, but upon ignition to 500-600° it becomes dark grey, and when then dissolved in water a black deposit of carbon is obtained. This results from occlusion of solvent in the precipitated sodium chloride. The error in weight of the precipitated sodium chloride, due to this cause, is variable and too large

<sup>1</sup> The work done in connection with this paper was suggested by H. H. Willard, and the preliminary work was carried out at the University of Michigan. The final work was done at the University of Illinois.

to be neglected. Precipitation at room temperature gave a similar result, but much less carbon was obtained. Wash solutions such as acetone, ether and carbon tetrachloride, are incapable of removing the occluded solvent from the precipitate. Ignition of the sodium chloride containing carbon in a stream of oxygen did not remove the impurity. The lower the temperature of the solution from which sodium chloride is precipitated, the less the tendency it shows to occlude solvent. When precipitated at -15° to -20° the dried and ignited salt contains no carbon but is pure sodium chloride.

*Effect of Acid Concentration Upon the Solubility of Sodium Chloride.*—Solutions of sodium perchlorate of known content were precipitated by the addition of butyl alcohol containing 20 per cent. of hydrogen chloride. A definite excess of hydrogen chloride was then added over that required for precipitation. After being heated to boiling, the precipitated samples were cooled to room temperature, filtered through asbestos, and washed with solutions of hydrogen chloride in butyl alcohol of the same strength as those from which the sodium chloride was precipitated. The precipitate was dried at 250°, ignited at 500-600° and the sodium chloride found, corrected for its carbon content, was compared with the amount present. The concentration of hydrogen chloride was gradually increased, until at 6 per cent. to 7 per cent. the solubility of sodium chloride reached a minimum of 0.6 mg. per 100 cc. This excess of hydrogen chloride can be obtained closely enough by adding to the solution of the perchlorate half as many cc. of 20 per cent. solution of hydrogen chloride in butyl alcohol, as there are grams of the solution. The wash solution is made in the same way.

The solubilities of the various salts involved are shown in the following tables:

TABLE II.

*Solubilities in Anhydrous Normal Butyl Alcohol at 25°.*

	G. per 100 g. solution.	Density 25°/4°.
LiClO <sub>4</sub>	44.23	1.1341
NaClO <sub>4</sub>	1.83	0.8167
LiCl	11.49	0.8713
NaCl	0.014 <sub>x</sub>	0.8060
	x 0.0116 g. per 100 cc.	

TABLE III.

*Solubility of Sodium Chloride Precipitated from Anhydrous Butyl Alcohol Containing 6 per cent. of Hydrogen Chloride.*

	NaCl taken G.	NaCl found G.	Vol. fil- trate and washings <sup>‡</sup> Cc.	Free HClO <sub>4</sub> present %	LiClO <sub>4</sub> present G.	Solubility of NaCl in 100 cc. G.
1	0.3021	0.3007	102	—	—	0.0014
2	0.3004	0.2989	110	—	0.1720	0.0014
3	0.3031	0.3020	102	—	—	0.0011
4	0.3510	0.3493	87	—	0.0356	0.0019
5	0.1549	0.1546	52	0.5	—	0.0006
6	0.1593	0.1590	55	0.5	—	0.0006
7†	0.1034	0.1027	43	0.5	—	0.0016
8	0.3505	0.3481	98	1.5	—	0.0024

<sup>‡</sup> Consisting of butyl alcohol containing hydrogen chloride and a little perchloric acid

† Alcohol as received, not dried or distilled.

It is evident from the above data that the solubility of sodium chloride is greatly reduced by the presence of hydrogen chloride. That of lithium chloride is, however, much less affected. The addition of 4.9 per cent. of hydrogen chloride reduced it from 11.49 g. to 9.60 g. per 100 g. of solution. No lithium chloride was precipitated when a 20 per cent. solution of hydrogen chloride in butyl alcohol was added to a 40 per cent. solution of lithium perchlorate in the same solvent. The solubility of sodium chloride is reduced from 11.6 mg. per 100 cc. in pure, dry butyl alcohol to 1.4 mg. by the addition of 6 per cent. hydrogen chloride and to 0.6 mg. per 100 cc. by the further addition of 0.5 per cent. of 70 per cent. perchloric acid. The reason for this latter decrease is not evident. More than 0.5 per cent. of perchloric acid increases the solubility. In unpurified and undried 6 per cent. hydrogen chloride—alcohol containing 0.5 per cent. of perchloric acid, the solubility rises to 1.6 mg. per 100 cc.

*Conditions Favouring Filtration.*—The higher the temperature of precipitation, the greater the ease of filtration. From a boiling sodium perchlorate solution in butyl alcohol, the sodium chloride precipitated is perchlorate solution in butyl alcohol, the sodium chloride precipitated is coarse, settles rapidly, and filters easily. From the same solution precipitated at room temperature, the precipitate is more gelatinous, settles slowly, and is difficult to filter and

wash. The same solution precipitated at  $-15^{\circ}$  to  $-20^{\circ}$  cannot be filtered.

Since it is desirable to utilise cold precipitation to prevent occlusion of solvent by the sodium chloride, solutions precipitated at  $-15^{\circ}$  to  $-20^{\circ}$  were heated to boiling and allowed to cool to room temperature before filtration. The precipitate of sodium chloride should be formed by adding, drop by drop, to the cold solution, 1-1.5 cc. of the hydrogen chloride—butyl alcohol reagent, the remainder to form a 6 per cent. acid—butyl alcohol solution being added rapidly. Under these conditions the precipitated sodium chloride, after boiling, settles rapidly, and after cooling to room temperature can be filtered clear, using a Gooch crucible. It is washed with a 6-7 per cent. solution of acid in butyl alcohol. If the concentration of acid is over 6 per cent., coagulation of the sodium chloride is less effective.

*Physical Constants of the Butyl Alcohol Used in the Method.*—In view of the results obtained by Winkler<sup>3</sup> in the use of isobutyl alcohol, a rather carefully purified *n*-butyl alcohol was employed in most of the work recorded in this paper. Winkler used isobutyl alcohol dehydrated over caustic potash and which had a boiling range of one degree, 106-107°. It was further specified that this fraction of the dried sample was necessary for good results. It will be shown later that drying only and no fractionation is required.

*Treatment of Filtrates from Sodium Chloride for Recovery of Lithium.*—The filtrates from the sodium chloride precipitate consisted of a butyl alcohol solution of hydrogen chloride and perchloric acid, lithium and a slight amount of sodium as perchlorate or chloride, the latter resulting from the almost negligible solubility of sodium chloride. The salts were recovered by evaporation of the solvent and volatile acids, converted to lithium and sodium sulphates, ignited and weighed. From this weight, corrected for the known amount of sodium sulphate, the amount of lithium was calculated.

Although the dilute solution of anhydrous perchloric acid and lithium perchlorate could be boiled without trouble, evaporation to dryness without first adding water resulted in a violent deflagration; 30 to 50 cc. of water was added to 50-100 cc. of the cold alcoholic solution and 2 immiscible layers were obtained. The under layer of water extracted most, if not all, of the products of solution from the upper alcoholic layer. When this mixture was evaporated on a steam-bath the alcoholic layer evaporated completely, leaving the greater part of the water solution of lithium and sodium perchlorates and perchloric acid. The organic matter remaining was eventually oxidised, and after the addition of sulphuric acid the evaporation was continued to dryness. The lithium sulphate was then dissolved in a little water, washed into a weighed platinum crucible, covered and heated over a ring burner to remove excess of sulphuric acid. The conversion of lithium perchlorate to lithium sulphate is more easily carried out without loss than conversion of lithium chloride to sulphate. The lithium sulphate was ignited in a muffle at 600° for 5 to 10 minutes, or to constant weight in case of large amounts. Samples thus treated were neutral and could be fused without loss in weight.

#### SEPARATION OF SODIUM AND LITHIUM.

When free from potassium, the mixed chlorides (free from sulphate) obtained by the J. Lawrence Smith or other method, are evaporated to dryness with excess of perchloric acid. A second evaporation is desirable if the amount is large. If potassium is present it is first separated by the usual perchlorate method and the filtrate, after addition of water, to avoid explosion, is evaporated to dryness. Since a definite amount of perchloric acid should be pre-

sent, it is desirable to remove first all excess of acid.

The mixed perchlorates of sodium and lithium free from perchloric acid are dissolved in anhydrous *n*-butyl alcohol using at least 15 g. or 18.5 cc. for each 100 mg. of sodium chloride present. The containing beakers may be conveniently weighed upon a small platform balance. The mixture dissolves readily if the alcohol is heated to boiling, which can be done with a burner over a wire gauze; 0.1 cc. of 70 per cent. perchloric acid is added and the solution is cooled to -15° by means of a freezing mixture. The sodium chloride is precipitated by adding from a buret, drop by drop, with constant stirring, 1-1.5 cc. of a 20 per cent. solution of hydrogen chloride in anhydrous butyl alcohol, after which the amount necessary to form a 6 per cent. solution is rapidly added (half as many cubic centimetres as there are grams in the solution to be precipitated). The precipitate of sodium chloride is then coagulated by heating the solution to boiling on a wire gauze with a free flame. After cooling to room temperature the sodium chloride is filtered on a weighed Gooch crucible and washed 8 or 10 times with a 6-7 per cent. solution of hydrogen chloride in butyl alcohol. (A rubber-tipped rod can be used in transferring the precipitate from beaker to crucible. It is well to preserve it by washing with a little acetone after use.) The sodium chloride is dried for one hour at 250° and ignited for 5 to 8 minutes at 600° in a muffle furnace (a free flame may be used but a very dull red must not be exceeded). A correction of 0.6 mg. for the sodium chloride remaining in each 100 cc. of filtrate and washings is added to the weight of sodium chloride found, to obtain the total sodium chloride present.

The filtrate and washings from the sodium chloride are diluted with one-third their volume of water (to avoid subsequent deflagration) forming 2 layers, and the whole is evaporated on the steam-bath in such a way as to avoid any condensation on the upper part of the beaker, which causes loss by "creeping." It is well to add 5 to 10 cc. of water at the end to make the removal of organic matter more complete before the perchloric acid takes effect. By such treatment a colourless residue of lithium perchlorate and perchloric acid can be obtained. If a slight brown colouration is present, remove the watch glass sup-

ports from the beaker and heat the covered beaker on a wire gauze to fumes of perchloric acid. If any brown colour remains adhering to the beaker walls after this treatment, it can be removed by brushing the walls of the beaker with the flame. If not enough perchloric acid is present to oxidise the last traces of organic matter, a few drops are to be added. When the brown colouration is removed, 0.5 cc. of conc. sulphuric acid is added, the watch glass replaced, and the acid fumed off, using either a hot plate or low flame and wire gauze. The beaker is then cooled, 5 to 10 cc. of water is added, and the cover glass and beaker walls washed. The lithium sulphate is then transferred to a platinum crucible previously ignited and weighed with its lid. The solution is cautiously evaporated to dryness and the covered crucible is heated, preferably by a ring burner, until every trace of acid is removed, after which it is heated to 600° in a muffle for 5 to 10 minutes. When the same treatment is carried out using a free flame and a very dull red heat, some reduction to sulphide often takes place, due to diffusion of the flame gases through the platinum. Fusing with a free flame to check the weight obtained by the above treatment is possible if the temperature is not too high or the treatment too long.

The weight of lithium sulphate is to be corrected for its sodium sulphate content by subtracting the weight of the solubility correction calculated as sodium sulphate, or 0.7 mg. per 100 cc. of filtrate and washings. A further correction to be applied is a blank for the reagents employed. This correction is found by precipitating a weighed sample of sodium chloride in the manner above described. One cc. of perchloric acid is ample for any ordinary quantity of salts to be converted, and the subsequent additions of 0.5 cc. each of sulphuric acid and perchloric acid are enough to provide excess. The weight of material obtained at the end of this process should be less than 1 mg. when corrected for the

sodium chloride solubility.

Gooch crucibles with 0.5 mm. holes are much better than those with large holes. Platinum Gooch crucibles with their much smaller perforations are still better. A heavy mat of asbestos is essential, and a perforated porcelain disc should be placed on it to prevent disturbance of the mat. If platinum-sponge filtering crucibles are used, weighing of the empty crucible should be made after the sodium chloride has been washed out with water, since spongy platinum is slightly attacked. Asbestos for use in filtrations with solutions of hydrogen chloride in butyl alcohol should be refluxed with some of this material in preparation for its use. The same crucible should be used many times over, and in such a case previous treatment of the asbestos with the acid-alcohol solution is not necessary. To show the effect of the solvent upon asbestos, the same crucible was used repeatedly, starting with untreated asbestos. The sodium chloride was washed out each time. The following successive weights were obtained: 26.6413, 26.6405, 26.6401, 26.6401, 26.6401. In order to avoid an additional operation the filtration with suction can be made directly from the crucible to a beaker by using a vacuum desiccator of the usual form but with a hole provided in the cover for the passage of a filtering tube and rubber stopper. In this way the beaker to receive the filtrate can be placed in the bottom of the desiccator. The filtering tube should have a small perforation in its side about an inch from the bottom to prevent spattering.

The filtrates were rapidly evaporated on the steam-bath by immersing the beaker in a copper capsule flanged at the top and fitted to the rings of the steam-bath so that condensation did not take place on the walls of the beaker or cover glass. This is very important because the alcoholic solution shows a strong tendency to "creep."

The value of the method was tested by a series of analyses of known mixtures, with the results recorded in the following table.

TABLE IV.  
*Separation and Estimation of Sodium and Lithium.*

Expt.	NaCl taken G.	NaCl found G.	Error G.	LiClO <sub>4</sub> taken G.	LiCl calc. G.	Li <sub>2</sub> SO <sub>4</sub> found G.	LiCl found G.	Error G.
1	0.1521	0.1519	-0.0002	0.4819	0.1920	0.2488	0.1919	-0.0001
2	0.1481	0.1478	-0.0003	...	...	...	...	...
3	0.1017	0.1017	0.0000	0.5534	0.2205	0.2860	0.2206	+0.0001
4	0.2027	0.2024	-0.0003	0.5295	0.2110	0.2736	0.2110	0.0000
5	0.1016	0.1016	0.0000	0.3004	0.1197	0.1558	0.1202	+0.0005
6	0.0217	0.0218	+0.0001	0.4455	0.1775	0.2315	0.1785	+0.0010
7	0.0502	0.0503	+0.0001	1.5354	0.6118	0.7929	0.6116	-0.0002
8§	0.1017	0.1019	+0.0002	...	...	...	...	...

§ Alcohol dried but not fractionated; b oiling range 112-118°.

The separation of sodium from very large amounts of lithium is accomplished by one precipitation (Expt. 7).

In case it is desired to avoid a cold precipitation (a step which requires but one short additional operation), the method can be applied exactly as described, omitting cooling to  $-15^{\circ}$  before precipitation, and adding the precipitant to the mixed perchlorate solution at nearly its boiling temperature. In this case the solubility of sodium chloride was found to be 1.6 mg. in 100 cc. of solvent. The carbon occluded by a precipitate of about 0.5 g. of sodium chloride is approximately 1.5-1.0 mg. under these conditions. The weight of sodium chloride in the precipitate can be determined by dissolving it in water, drying the crucible with its carbon impurity, and weighing after filtration rather than before.

#### SUMMARY.

1. A method is described for the separation of sodium and lithium based upon the precipitation of sodium chloride from a solution of the perchlorates in anhydrous *n*-butyl alcohol by the addition of an alcoholic solution of hydrogen chloride.

2. Conditions affecting the accuracy of the process were studied and the accompanying errors eliminated.

3. The solubilities of the anhydrous perchlorates and chlorides of lithium and sodium in anhydrous *n*-butyl alcohol at  $25^{\circ}$  are given.

4. A table is given showing the density and composition of solutions of hydrogen chloride in butyl alcohol.

5. Test analyses show that one separation gives accurate results even in the presence of large amounts of lithium.

*Ann Arbor, Michigan and Urbana,  
Illinois.*

(From the "Journal of the American Chemical Society," p. 2816, 1922.)

#### GENERAL NOTES.

##### BRITISH STANDARDS FOR ELECTRICAL MACHINERY.

The British Engineering Standards Association announces the withdrawal of British Standard Specification 72-1917, from circulation. This document is now under revision, and will be divided into the following sections, each of which will be issued as a separate publication.

(a) Industrial machines (B.S.S. 168-1923) has already been published, whilst (b) Large machines, (c) Transformers, (d) Rotary Converters, and (e) Traction motors are in course of preparation. — (From the "Board of Trade Journal," July 12, 1923.)

##### CONDENSED MILK INVESTIGATION.

The Food Investigation Board of the Department of Scientific and Industrial Research has issued Special Report No. 13, under the title of "Studies in Sweetened and Unsweetened (Evaporated) Condensed Milk," by W. G. Savage, M.D., B.Sc., and R. F. Hunwicke, B.Sc., A.I.C.

The Report has been prepared by the Canned Foods Committee of the Food Investigation Board, and deals chiefly with the bacteriological problems involved in the successful condensation and canning of milk.—(From the "Board of Trade Journal," July 12, 1923.)

##### CANADIAN NATIONAL EXHIBITION.

In a recent dispatch, H.M. Trade Commissioner at Toronto reports optimistically of the probable British participation in the Canadian National Exhibition, to be held in that city from August 25 to September 8 next.

The British displays may be classified under three headings:—

(i) Private exhibits, which are far more numerous this year than previously.

(ii) The collective exhibit organised by the Federation of British Industries, which is understood to have been well supported.

(iii) The Propaganda and Samples Bureau, maintained for the Department of Overseas Trade by H.M. Trade Commissioner, on which firms will display trade catalogues and table samples. It is understood that at least 40 British firms will avail themselves of the opportunity offered by this Bureau.

In connection with the rapid growth of the Canadian National Exhibition, it is reported that the Cuban Government is considering a recommendation to vote a sum of 50,000 dols. for the erection of a permanent pavilion to house an annual Cuban exhibit at Toronto.—(From the "Board of Trade Journal," July 12, 1923.)

In the House of Commons, recently, Mr. Attlee asked the President of the Board of Trade whether he was aware that the British Dyestuffs Corporation, Limited, charged 10 per cent. commission on reparation dyestuffs, whereas, when the distribution was undertaken by the central importing agency, only 2½ per cent. was charged; and for what reason was this high rate of commission permitted?

Sir P. Lloyd-Greame replied: I am not aware that the British Dyestuffs Corporation charge 10 per cent. commission on reparation dyestuffs, and would refer to an answer which I gave on this matter on December 4 last, to the effect that the Corporation receives a commission of 6½ per cent. on the actual turnover plus a further 1 per cent. for guaranteeing accounts, and a grant, which is limited in amount, towards the charges which they incur relating to the importation of the dyestuffs. The Central Importing Agency undertook the duty of importing and distributing the dyestuffs for a commission of 3½ per cent., the rate to be adjusted if prices fell, but this charge proved to be inadequate, and was considerably increased with the approval of the Treasury by various allowances made to the Central Importing Agency upon the final adjustment of their accounts.

Mr. Attlee further asked the President of the Board of Trade whether he was aware of the high prices charged for reparation dyestuffs by the British Dyestuffs Corporation, Limited; that the price of diamine fast yellow F.F., a dye for which there was no satisfactory British substitute, had been raised from 4s. per lb. to 7s. 6d. per lb., and to 10s. per lb., although this dye could be imported from Germany for 4s. 6d. per lb.; and of the discontent aroused by this action among colour users; and what action he was prepared to take in the matter?

Sir P. Lloyd-Greame said: No complaint about the price of this dyestuff has been received by the Board of Trade, but the arrangements as to the pricing of reparation dyes are being reconsidered, and the price of this particular dye will come under review.

Major-General Sir Robert Hutchinson asked the President of the Board of Trade whether he was aware that British importers of lithopone from Germany who made contracts before February 1 found it almost impossible to get delivery of their goods, because the French authorities would not

issue export licences, even after the payment of the French 7 per cent. duty, and that although the French authorities, under pressure, agreed to issue export licences, they, in fact, put every obstacle in the way of British traders receiving these licences; and what could he do in the matter to protect British trade interests?

Sir P. Lloyd-Greame said: The answer to the first part of the question is in the negative. If the hon. and gallant member will furnish me with particulars of the cases which he has in mind I will make inquiry.

## CORRESPONDENCE.

### THE COLOURING OF POISONS.

*To the Editors of THE CHEMICAL NEWS.*

SIR,—In the interests of public safety, it will be unfortunate if a recent decision of the General Medical Council be accepted as the final word in the highly important question of colouring deadly poisons. The facts are simple. After careful experimenting by British dyemakers and pharmacists, the Pharmaceutical Society of Great Britain recommended Brilliant Green to the Privy Council as a colouring for a preparation of strychnine. The Privy Council forwarded the suggestion to the General Medical Council as the body who could say whether Brilliant Green would interfere with the healing properties of the strychnine preparation in question. Thereupon the General Medical Council unanimously condemned the proposal, and that for six reasons, only two of which can be said to have a remote connection with the curative aspect of the question, namely, that, in certain mixtures, Brilliant Green undergoes colour changes which "might be objectionable" to patients, and that a coloured solution "would be objectionable" for hypodermic injection.

The four other points made were: (1) that it was only proposed to colour one strychnine preparation; (2) that risk would arise from keeping coloured solutions side by side with uncoloured; (3) that, the preparation being uncoloured in other countries, difficulties of an international kind would arise; and (4) that the question was a general one and should not be determined in the case of a single preparation of a single poison.

These four objections may be just or they may not. What I do submit is that they are matters of policy to be determined by Parliament in open debate rather than settled autocratically by the most conservative of our trade unions.—Yours, &c.,

JAMES SEXTON.

House of Commons, S.W.1.

July 16, 1923.

### NOTICES OF BOOKS.

*Quantitative Chemical Analysis and Inorganic Preparations*, by R. M. CAVEN, D.Sc. (LOND.), F.I.C. Part I. Pp. VI. + 156. London: Blackie & Sons, Ltd., 50, Old Bailey, E.C. 1923. 3s. 6d. net.

The author has aimed at including in one volume all the essential practical exercises that a student should carry out. He has not included any superfluous matter—at least in the first part now under review.

Part I. includes a description of the preparation of certain typical salts and their gravimetric analysis, followed by exercises in volumetric analysis. It is intended that Part II. will contain a more extensive selection of preparations.

In general, the book follows the lines that have been found most suitable in presenting the subject to students. It possesses, however, one or two features that call for special mention. The introductory instructions are particularly well presented, and it is to be hoped that all students using the book will master them at the beginning of the course.

Another point of interest is the use of standard oxalic acid as the basis of standardisation in acidimetry and alkalimetry. By following this procedure, the teacher has a good opportunity to press home a number of interesting theoretical and practical points. It might be pointed out here that the short note on the Use and Theory of Indicators does not go very far and seems inadequate.

Also, whilst most of the matter in the section on preparations is good, the method suggested for ferrous ammonium sulphate could be much improved.

The book, as a whole, fulfils its intention for the use of students who have passed the elementary stage, and it will prepare such students, in practical work, up to degree standard.

### LITERARY INTELLIGENCE.

Volume II., Part II. of Molinari's "Organic Chemistry" will shortly be ready. This volume completes the whole section of the work, thus making available a comprehensive treatise covering the whole ground of Industrial Chemistry, both Inorganic and Organic.

The new part contains over 300 illustrations, and deals with the subjects of Esters, Oils and Fats, Sugars and other Carbohydrates, Cyclic Compounds, Dyestuffs, Textile Fibres, Proteins, etc.

The publishers are Messrs. J. & A. Churchill.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 17681—Finch, G. I.—Process for recovering ammonia from gases or vapours. July 7.
- 17130—Lilienfeld, L.—Manufacture of cellulose solutions. July 2.
- 17466—Soc. Chimique des Usines du Rhone.—Preparation of diethylchloracetamide. July 5.
- 17388—Soc. of Chemical Industry in Basle.—Manufacture of alkaline-earth metal compounds of the organic phosphorus compound in milk casein. July 4.

#### Specifications Published this Week.

- 173750—Brynes, C. P.—Partial combustion methods for treating aliphatic hydrocarbons.
- 199475—Lessing, Dr. R.—Manufacture of neutral sulphate of ammonia.
- 199607—Westermann, J. T.—Process for manufacturing pure sodium chloride.
- 181388—Chemische Fabrik Griesheim Elektron.—Process of the production of basic magnesium carbonate.

#### Abstract Published this Week.

- 197863—Phosphorus pentoxide.—Threlfall, Sir B., of Oakhurst, Church Road, Edgbastor, Birmingham.

Phosphorus pentoxide made by burning phosphorus in a stream of dry air is condensed at a temperature of 125 to 200° C. in a compact, crystalline form. To avoid the presence of a small amount of the amorphous, bulky variety a portion of the vapour at about 160° C. is led through a filter containing glass wool to a second condensing chamber.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3303.

## X-RAY SPECTROSCOPY AS A MEANS OF QUALITATIVE AND QUANTITATIVE CHEMICAL ANALYSIS.

By D. COSTER.

The X-ray emission from the anticathode of an X-ray tube consists of two essentially different parts: (1) The heterogeneous radiation, or the "white" X-ray light, the nature of which depends only on the tension used and not on the material of the anticathode; (2) The characteristic radiation, or the "line spectrum," which characterises the elements present on the anticathode. The

X-ray line spectra have a much simpler structure than the optical line spectra. The characteristic X-ray spectra of the different elements are built up in nearly the same way, which is due to the great similarity of the inner groups of electrons of the atom for the different elements. They consist of but very few strong lines and a relatively small number of weaker lines. For the X-ray lines the following simple relation holds: the square root of the frequency of a definite line is to a first approximation proportional to the atomic number of the emitting element. Roughly speaking, we could say: If the X-ray spectrum of a definite element is known, those for the next elements with higher atomic number are found by shifting the whole group of lines a certain amount to the short wave-length side. This fact may be illustrated by the following figures.

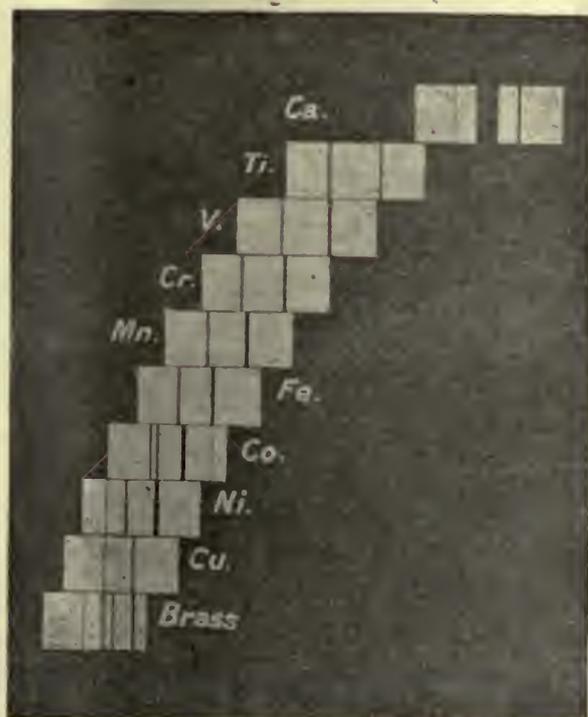


Fig. 1.

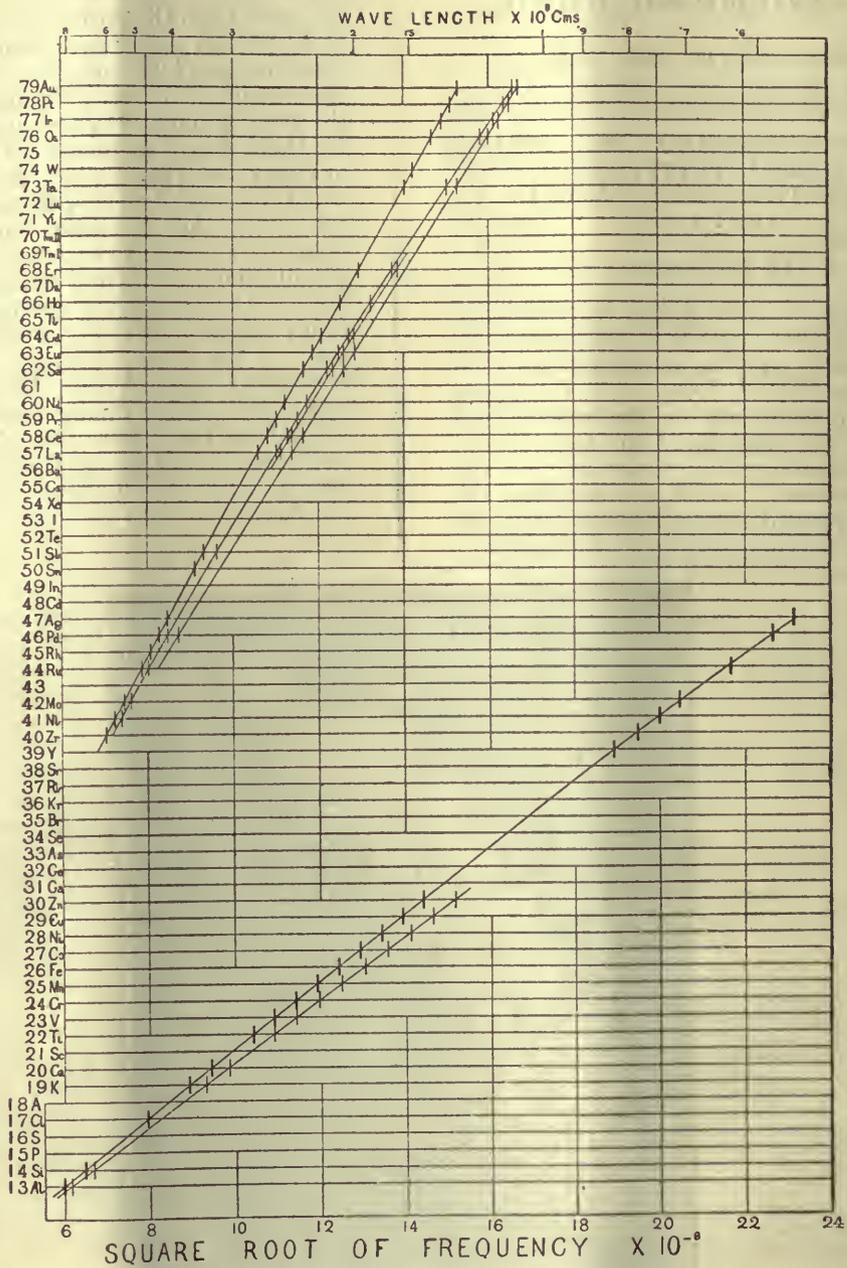


Fig. 2.

Fig. 2 gives the square roots of the frequencies of some lines of the K-series (ordinates) as a function of the atomic number (abscissæ). Fig. 1 gives the photographs of the lines for the same series for some lighter elements (both figures have been taken from a paper by Moseley<sup>1</sup>). As appears from the above, the atomic number of an element is strictly determined by its X-ray spectrum. As we know, Moseley, in his fundamental investigations of the high frequency spectra, was able to determine in this way the number of elements between Ba and Ta. Whereas, in consequence of the exceptional behaviour of the rare earth metals, no direct information in this matter could be obtained from Mendelejeff's table.

Due especially to the work done in the laboratory of Prof. Siegbahn, the X-ray spectra of the elements Na-U are known rather completely. Following Barkla's nomenclature of the characteristic X-radiation the lines have been classified in different groups or series which are called K-, L-, M-, and N-series. The range of wave-lengths which can be measured in the present state of X-ray spectroscopy lies between 13.5 and 0.1 Å-units. As a consequence of this, the K-series of the lighter elements could only be measured as far down as Na, the L-series is only known for the elements of higher atomic number than Co, whereas the M-series, as yet, has been found only for the elements of higher atomic number than Dy, and the N-series only for Bi, Th, and U.<sup>2</sup>

As a chemical element is unambiguously determined by its X-ray spectrum, X-ray spectroscopy may be used as well as optical spectroscopy, as a means of identification of elements. For this purpose the former

has even some important advantages: (1) As the X-ray spectra are much simpler than the optical spectra, the identification of the lines meets with less difficulties; (2) In X-ray spectroscopy it is of no importance in what mixtures or compounds the element in question occurs; (3) One per cent. of a certain element, in a preparation of which only 1 milligram is available, is enough to be detected.<sup>3</sup>

It may be pointed out, however, that in general some faint X-ray lines do not suffice to determine a certain element, even if their position nearly coincides with that expected for the element in question. Though, as is stated above, the number of X-ray lines is very limited, in the last few years several investigators have succeeded in establishing the existence of a rather large number of fainter lines. Moreover, as usually rather high tensions are used, not only the spectrum of first order, but also that of second and third, and in some cases even of still higher order may appear.<sup>4</sup> As also very small impurities of the anti-cathode material and of the substance under examination give their characteristic X-ray spectrum, in most cases there are several possibilities for the identification of a given line. In order to avoid erroneous conclusions, regard must therefore be taken not only to the wave-lengths of the lines, but also to their typical behaviour, especially as regards the relative intensity of the lines belonging to the same element.

In one respect, however, X-ray spectroscopy might be of more use for chemistry than optical spectroscopy, in that it may also be applied successfully to quantitative analysis. It was used for the first time for this purpose by Hevesy and the author

<sup>1</sup> *Phil. Mag.*, 1913, XXVI., 1024; 1914, XXVII., 703. Though in Fig. 1 the nomenclature of the elements 69-72 is not wholly up-to-date, I thought it of great historical interest to reproduce the figures as they are found in the original papers.

<sup>2</sup> See M. Siegbahn, *Jahrbuch für Radioaktivität*, 1922, XVIII., 240. Publications of later date which are not mentioned in Siegbahn's summarising article are: M. Siegbahn and V. Dolejšek, *Zeitschrift für Physik*, 1922, X., 159; D. Coster, *Phil. Mag.*, 1922, XLIII., 1070 and 1922, XLIV., 546; Hjalmar, *Zeitschrift für Physik*, 1923, XV., 65.

<sup>3</sup> *Methods and apparatus have been thoroughly discussed by M. Siegbahn Jahrbuch der Radioaktivität*, 1916, XIII., 296, and 1922, XVIII., 240.

<sup>4</sup> According to Bragg's relation:  $n\lambda = 2d \sin \theta$  (here  $\theta$  is the glancing angle,  $d$  the grating constant,  $\lambda$  the reflected wave-length, and  $n$  an integer) corresponding to different values of  $n$  different values of  $\lambda$  are related to a definite glancing angle.  $n = 1$  corresponds to the first order spectrum,  $n = 2$  to the second order spectrum, etc. How far the spectra of higher order appear depends on the tension used and the analysing crystal.

during an examination of the occurrence of the new element hafnium<sup>5</sup> in zirconium minerals and the investigation of its chemical properties. The main feature of the method is the addition to the substance to be examined of a known quantity of an element with an atomic number in the neighbourhood of that of the element under consideration and the determination of the X-ray spectrum of the mixture. By comparison of the intensity of the lines of the added element to that of the corresponding lines of the element under investigation an estimation of the concentration of the latter element may be obtained. The reliability of the method appears from the following considerations. The energy of an X-ray line is proportional to the number of atoms of the corresponding element in the anticathode spot. In the case of two elements adjacent in the periodic table, the configuration of the inner electrons of the atom is very nearly the same. We may, therefore, assume that the ratio of the energies of two corresponding lines of such elements in first approximation is the same as that of the numbers of radiating atoms belonging to each of them.

Two objections could be raised against the method. (1) The critical exciting tension of a definite line is not the same for different elements. Using a tension which is much higher than the critical tension of the lines for the elements in question, this difference may be neglected<sup>6</sup>. (2) Another objection could be made against the practical application of the method. By sputtering or evaporation, part of the atoms present in the anticathode spot will disappear during the course of an exposure. In general this will give rise to a change in the ratio of the quantities of the different elements present on the anticathode. Errors due to this circumstance, however, may be avoided by a suitable choice of the conditions of experiment (small current densities in the anticathode spot). Only in a few exceptional cases, e.g., if mercury or iodine

compounds are to be investigated, the method would not lead to the right results.

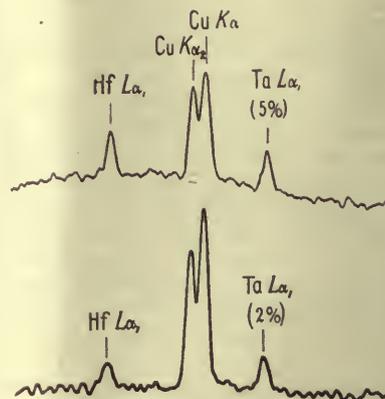


Fig. 3.

Figure 3 shows how the hafnium content in zirconium minerals was determined. The figure represents a photometer curve of the blackening of the photographic plate taken with the Moll microphotometer<sup>7</sup> of the firm Kipp (Delft, Holland). The uppermost curve is taken from a plate of a zirconium mineral from the Ural. The hafnium content appears to be a little more than 5 per cent. The copper lines are due to the copper anticathode. The zirconium  $K\alpha$  lines which in second order lie nearly on the same place as the hafnium  $La$  lines, could not appear on the plate, as the tension used during the exposure was less than the critical tension for the zirconium lines, i.e., 18,000 volts. The other curve represents the blackening of a photograph of a zirconium mineral from Brazil. The hafnium content appears to be a little smaller than 2 per cent.

In the same way the chemical properties of hafnium were studied. Our former investigations had already shown that in nearly all zirconium minerals a rather large percentage of hafnium is present. From this we might conclude that the chemical properties of hafnium are closely related to those of zirconium. This conclusion was firmly established by a further investigation. The method used may be illustrated in the following example. In order to determine the solubility of hafnium phos-

<sup>5</sup> *Nature*, Feb. 10, 1923. See also G. Hevesy, *The Chemical News*.

<sup>6</sup> In this connection it may be pointed out that the intensity of the characteristic X-ray spectrum is in first approximation proportional to the second power of the difference of the tension used and the critical tension.

<sup>7</sup> W. J. H. Moll, *Proceedings Phys. Soc. London*, 1921, XXXIII., 207.

phate compared with that of zirconium phosphate, a solution of a mixture of zirconium and hafnium was precipitated with sodium phosphate in 11 equal fractions. The original mixture contained about 4 per cent hafnium; 10 per cent Ta was added to each of the different fractions, and then the X-ray spectra were investigated. Figure

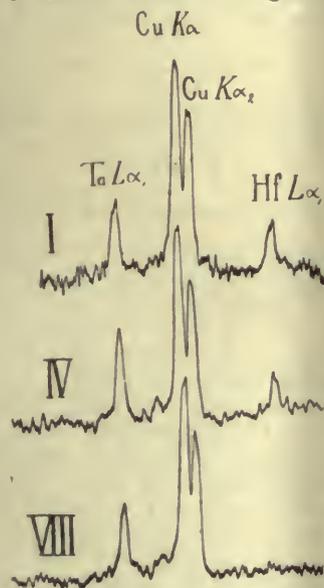


Fig. 4.

4 gives the photometer curves of the spectra of the 1st, 4th, and 8th fraction. These curves clearly show that the solubility of hafnium phosphate is considerably less than even that of zirconium phosphate.

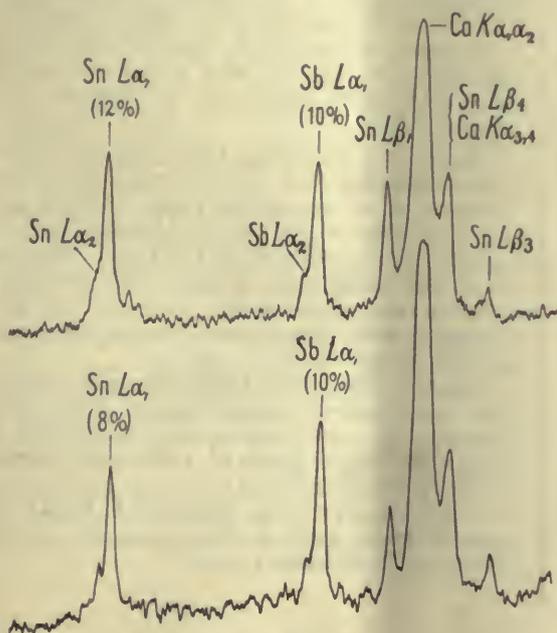


Fig. 5.

Fig. 5 gives an idea of the sensibility of the method. Two artificial preparations were made of  $\text{CaSO}_4$  mixed with  $\text{SnCl}_2$  and  $\text{Sb}_2\text{O}_3$ . Both preparations contained 10 per cent. antimony. To the first 12 per cent. ten was added, to the other 8 per cent. The photometer curves express very well the real state of things. It may be pointed out that the above example was not at all chosen so that it should give a too favourable impression of the reliability of the method. Indeed, antimony oxide sublimates very soon, and when the preparation was heated in the Bunsen flame before the exposure, the antimony appeared to have decreased by about 30 per cent. relatively to the amount of ten. Therefore, in exposing the plates, a rather small current was used and the anticathode was cooled effectively.

Evidently it is possible to improve the sensibility of the method. We will discuss some sources of error which were to be taken into consideration for obtaining a larger accuracy. (1) The photographic plate has not the same sensibility at different places. Errors of this origin could be avoided by determining the photometer curves at different heights of the plate and eventually by taking more than one plate of the same preparation. (2) The different lines appearing on the photographic plate are reflected by different parts of the crystal and in general the reflecting power of the crystal will not be the same at different places. (3) The different lines correspond to different parts of the anticathode spot for which in general the intensity of radiation will not be the same. The last two errors could be avoided for the greater part by constructing the apparatus in such a way that only a very small angle was exposed at the same time. In this case only a definite part of the crystal is used, the radiation coming from a definite part of the anticathode spot. As it is necessary to photograph more than one line on the same plate the crystal was to be turned during the exposure.

In order to obtain a greater accuracy it would also be desirable to make the amount of the comparison element as exactly as possible equal to that of the investigated element, which, of course, can only be done by repeated trials. In proceeding in this way, however, we should miss one of the greatest advantages of X-ray analysis, *i.e.*, its rapidity. Therefore in this form it should only come into consideration for elements like zirconium and hafnium, for which quantitative analysis meets with great difficulties. But if a great accuracy is

not wanted in the first place, *e.g.*, in the case of investigations of minerals, the method as it was used in our hafnium investigation works very quickly, having at the same time a high reliability. In this connection it may be pointed out that it is not at all necessary to take photometer curves of all the plates. After some experience, it is not difficult to estimate rather accurately the relative intensity of lines with the eye. Moreover a relatively small difference in the blackening of the lines reveals itself clearly as a phase-difference in the appearance of the lines during the development of the plate.

As is shown above, X-ray analysis gives a means of rapid determination of the nature and the amount of the elements occurring in a preparation. It may, however, also be used in an investigation of the physical and chemical state of these elements. The method described above is founded on the analysis of the characteristic X-ray spectrum of the investigated element by reflection on a crystal plane of a crystal with known space grating constant, *e.g.*, calcite, rocksalt or gypsum. But we can conversely also try to determine the crystal structure of our preparation with the aid of monochromatic X-ray light of known wave-length. About this side of X-ray analysis I will only make some remarks which could be of interest in connection with the above. Ordinary qualitative analysis is able to inform us that a certain preparation contains, *e.g.*, calcium and potassium and a chloride and a nitrate, but this analysis does not directly give the further information as to whether we have a mixture of calcium nitrate and potassium chloride, or of calcium chloride and potassium nitrate. An examination of the crystal structure, however, will throw light upon this question also. For this purpose the most adequate method is the "pulverised crystal method."<sup>8</sup> Naturally it is not possible to use a diagram of a crystal mixture for calculating the different crystal structures which are present in the mixture, but this is not necessary. The only thing we want is a collection of standard diagrams of the crystal structures which may be supposed to be present in the mixture. By a

comparison of the diagram of the mixture and the standard diagrams it is easy to see which crystals are present and which not. In this way Dr. A. Hadding, of Lund—as he kindly told me—has used X-ray analysis to determine the components of dense mineral ores and other mineral aggregates.

## ORGANIC COMPOUNDS OF ARSENIC.

### PART I.

By R. F. HUNTER, F.C.S.

The organic compounds of arsenic are some of the most interesting and valuable substances, both from the point of view of academic interest and from that of therapeutic value, and hence a brief survey of our knowledge might be given.

The subject carries us back to the year 1760, when Cadet produced his "fuming liquid" by the distillation of arsenious acid with sodium acetate in equal proportions by weight: Two liquids appeared in the receiver used in the distillation, the more volatile compound exhibited acid properties while the less volatile compound was a red-brown liquid which filled the receiver with fumes. Both components had a most sickening odour, resembling to some degree the odour of garlick. The heavier of the two liquids, that is to say, the red-brown compound exhibited spontaneous inflammability when an attempt was made to pour it from the receiver at ordinary temperature. Madet and Durande, who subsequently investigated the reaction, showed the heavy liquid to possess the viler stench and to be the component possessing spontaneous inflammability.

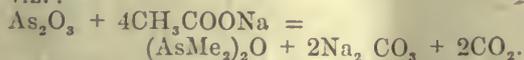
The most sickening foetid odour of the compound deterred investigators from the subject for nearly eighty years. This is not so surprising when we consider the lack of means for experiment of the time, coupled with the stupefying odour which produced nausea and unbearable irritation of the nasal mucous membrane, which the compound possessed.

In the years 1837-1843, Bunsen carried out his classical researches on this compound. The preparation was repeated on a large scale, 500 gms. of both constituents being distilled together:

Analysis gave the formula  $C_4H_{12}As_2O$ , and Bunsen showed the compound to be tetra-methyldiarsine oxide,

<sup>8</sup> P. Debye and Scherrer, *Phys. Zs.*, 1916, XVII., 277; A. W. Hull, *Phys. Review*, 1917, X., 661.

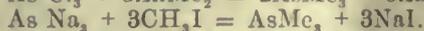
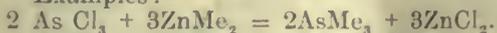
$(\text{CH}_3)_2\text{AsOAs}(\text{CH}_3)_2$ ,  
and the reaction to be our usual  
test for an acetate in minute quantities,  
viz. :—



The free radical cacodyl or dimethylarsene was subsequently isolated by the action of zinc shavings on the chloride of cacodyl, the reaction carried out in an atmosphere of  $\text{CO}_2$ . This is only a brief historical survey, and the complete accounts can be found in the references at the end of the article.

Aliphatic arsenicals, such as methylarsines, etc., have been prepared by the usual methods given in text books of organic chemistry, viz., such reactions as the action of zinc alkyls on arsenious chloride, alkyl halides on sodium arsenide, etc.

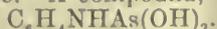
Examples :—



The compounds of several series of this type have been studied, for instance, Ethylarsines, Propyl, Allyl, and Butyl, and amyl arsines and their derivatives have been described by various workers.

The aromatic compounds are of more interest to us, however, from the point of view of their closer relationship to the important medicinal compounds of arsenic such as salvarsan, etc., which are of great importance in the treatment of protozoal diseases.

As far back as 1868 Bechamp found that arsenic could react with aniline without oxidation of the base, he obtained apart from his other products, such as dyes of magenta type. A compound,



It is remarkable that only within the last ten years or so have we come to regard the acid as having the constitution which was assigned to it by its discoverer.

The sodium salt was introduced into medicine under the name of "atoxyl," which was much used at one time as a cure for sleeping sickness. The compound was used in the form of intravenous injections. It was a compound remarkably fatal to the trypanosomes of sleeping sickness, but suffered from the disadvantage that the patient very often exhibited symptoms of arsenical poisoning after such an injection, the poisonous effects being cumulative such that they could finally give rise to complete blindness and kidney complications.

Hosts of researchers in the field of aromatic arsenicals have produced a large

number of compounds of varying importance.

The classes of compounds produced might have been divided as follows :—

(1) Benzene derivation with one aromatic nucleus attached to one arsenic atom.

Examples: Phenylarsenious chloride,  $\text{C}_6\text{H}_5\text{AsCl}_2$ , compounds, such as the methyl ethyl phenyl esters of phenylarsenious acid :

Phenylarsenic acid,  $\text{C}_6\text{H}_5\text{AsO}(\text{OH})_2$ , its salts, esters and halogen derivatives, but

Arsenobenzene,  $\text{C}_6\text{H}_5\text{AsAsC}_6\text{H}_5$ , is the most interesting compound of this class owing to its relation to salvarsan.

(2) Benzene derivatives with two aromatic nuclei attached to one arsenic atom, examples of which are diphenylarsenious chloride, phenylcacodyl,  $(\text{C}_6\text{H}_5)_2\text{AsAs}(\text{C}_6\text{H}_5)_2$ , diphenylarsine and its derivatives.

(3) Benzene derivatives with three aromatic nuclei attached to one arsenic atom. Triphenylarsine,  $\text{Ph}_3\text{As}$ , is simplest example.

(4) Toluene derivatives with one aromatic nucleus attached to one arsenic atom.

Examples of this are o-Tolyarsenious chloride, o-Tolyarsenious oxide, o-tolyarsenious acid, and the corresponding m and p compounds.

We have also mixed tertiary arsenic with a tolyl radical, an example of which is p-tolydimethyl arsine.

(5) Toluene derivatives with two or three aromatic nuclei attached to one arsenic atom.

These we further sub-divide into triaryl and diaryl series, examples being tri-p-tolyarsine and Di-p-tolyarsenious chloride.

(6) Benzyl derivatives, of which tribenzylarsine,  $\text{As}(\text{CH}_2\text{C}_6\text{H}_5)_3$ , is an example.

(7) Aromatic arsenicals containing higher aryl groups: Compounds such as m-xylylarsenious chloride; oxide, sulphate, etc., are examples.

(8) Arsenical derivatives of naphthalene, these are of peculiar interest, and examples are:  $\alpha$ -Naphthylarsenious Chloride,  $\text{C}_{10}\text{H}_7\text{AsCl}_2$ ;

Arsenic  $\alpha$ -naphthalene,  $\text{C}_{10}\text{H}_7\text{AsAsC}_{10}\text{H}_7$ ;

$\alpha$ -Naphthylarsenic acid,  $\text{C}_{10}\text{H}_7\text{AsO}(\text{OH})_2$ ;

$\beta$ -Naphthylarsenic acid,  $\text{C}_{10}\text{H}_7\text{AsO}(\text{OH})_2$ .

(9) Benzarsenic acids and derivatives which are further sub-divided into:

(a) Toluene series.

(b) Xylene series.

(c) Pseudo cumene series.

p-Benzarsenic acid,

$\text{CO}_2\text{HC}_6\text{H}_4\text{AS O (OH)}_2$ , is an example of the first, and phenylditolyarsineoxidetetracarboxylic acid, triphenylarsineoxidetetracarboxylic acid, are examples of the second, and phenyldixylylar-sineoxidedicarboxylic acid and phenylditolyarseneoxidetetracarboxylic acids are examples of the third.

(10) Betaines of Aromatic Arsenicals.

Phenyldiethylarsenicbetainehydrochloride, and triethylarsenibenzobetaine are good examples.

(11) Nitro derivatives of aromatic arsenicals, compounds such as m-nitrophenylarsenic acid, m-nitrophenylarsenicals, bro-fide sulphides, sesquisulphide, dinitro-diphenylarsenious sulphide, chloride, etc., are examples.

Of particular interest in the group are the reduction products of 3-nitro-tolyarsenic acid:

3:3 dinitro arsenic p-toluene.

3-nitro-4-tolyarsenious sulphide.

3-amine-4-tolythioarsenic acid, etc.

We have now to consider the two classes, compounds which are of immense importance in medicine, and which will be dealt with under the titles of Atoxyl and its derivatives, Salvarsan and its derivatives.

## RELATIVE DETERMINATION OF THE ATOMIC WEIGHT OF CHLORINE IN BAMLE APATITE.

BY MARGOT DORENFELDT.

### INTRODUCTION.

This work was undertaken at the suggestion of Dr. Ellen Gleditsch in connection with an investigation carried out by Gleditsch and Samdahl,<sup>1</sup> the object being to determine whether, in an old mineral which has not been in contact with water, the two chlorine isotopes of atomic weights 35 and 37 occur in the same proportion as in ordinary chlorine. The mode of attack was to compare the specific gravities of saturated solutions of sodium chloride, one solution being made from ordinary sodium chloride and the other from Bamle apatite, the method being similar to that described by Fajans and Lambert.<sup>2</sup>

<sup>1</sup> Gleditsch and Samdahl, *Compt. rend.*, 1922, CLXXIV., 746. *Arch. Math. Naturvidensk.*, 1923. XXXVIII.

<sup>2</sup> Fajans and Lambert, *Z. anorg. Chem.*, 1916, XCV., 297.

### APPARATUS AND MATERIALS.

The pycnometer was an exact copy of one described by Fajans and Lambert,<sup>2</sup> a modified Sprengel-Ostwald type. The temperature variations of the thermostat cannot be given accurately, but a 0.1° thermometer showed no change. The glass test-tubes in which the solutions were rotated in the thermostat were of thick glass, 14 cm. long, and of 22 mm. internal diameter. The clean tubes and the rubber stoppers were soaked in warm brine solution for 12 hours, after which treatment they were carefully rinsed. The balance was a Bunge with a sensitiveness of 0.4 mg.; no mirror was used, but  $\frac{1}{4}$  divisions could easily be read.

The "ordinary sodium chloride" was a commercial highly purified preparation which was further purified. A saturated solution was treated with chlorine, the excess chlorine removed by boiling, the salt precipitated with hydrogen chloride, recrystallised several times, ignited, and then recrystallised several more times. All final crystallisations were made in platinum with twice-distilled water, the second time from alkaline permanganate.

The apatite was from the Odegaarden mines in Bamle, and was comparatively rich in chlorine, but the presence of considerable fluorine made it difficult to obtain a preparation free from silica. It was heated with 70 per cent. c.p. sulphuric acid and the acid distillate of hydrochloric, hydrofluoric and sulphuric acids and silicon tetrafluoride was neutralised with a highly purified commercial sodium carbonate. The precipitated silica was removed, and after 3 crystallisations the salt was divided into 2 portions, from 1 of which was made a saturated brine solution and from the other was generated a stream of hydrogen chloride which was brought to the surface of the brine solution. The precipitate, dried by suction, was heated to redness in platinum, dissolved, filtered, recrystallised 7 times, ignited again, dissolved and filtered, and then recrystallised 5 times.

### SPECIFIC-GRAVITY DETERMINATIONS OF THE SATURATED SOLUTIONS.

The two salt solutions, one from ordinary sodium chloride, the other from apatite, were evaporated until crystallisation began. The warm solutions were transferred to the tubes, and when cool, the tubes were tightly closed with rubber stoppers.

After 3 days' rotation the first weighings of the filled pycnometer were made, No. 1 in the table below. The "apatite sodium



chloride" solution was slightly cloudy, the numerous recurring opalescence must have been due to traces of fluoride. Baryta water was added, whereupon a distinct turbidity appeared, and the solution was filtered. The excess of barium hydroxide was precipitated by carbon dioxide gas, the excess of carbon dioxide driven out by boiling, and the solution filtered. The filtrate was neutralised with a few drops of "apatite hydrochloric acid," evaporated to saturation and precipitated with alcohol. The ignited powder was reprecipitated with alcohol and then crystallised several times. The "ordinary sodium chloride" was evaporated to dryness, heated to redness, dissolved, filtered, and recrystallised several times.

After 3 days' rotation another weighing was made, No. 2 in the table. The specific gravity of the "ordinary sodium chloride" being unchanged shows the preparation to

TABLE I.  
SPECIFIC GRAVITIES OF SATURATED  
SOLUTIONS.<sup>†</sup>

Expt.	"Ordinary Sodium Chloride"		"Apatite Sodium Chloride"
	Temp., 18°		
1	1.202791	} 1.202791	1.203698
2	1.202790		1.204691
3	.....		1.203597
4	.....		1.202791
5	.....		1.202857
6	1.202867		1.202852

<sup>†</sup> Vacuum corrections were applied to all weighings, taking 8.4 as the specific gravity of the brass weights by the usual formulae.

be pure, but the "apatite sodium chloride" was again treated as above, giving value No. 3. This solution was then evaporated to dryness, ignited, and recrystallised thrice. Weighing gave value No. 4, 1.202791, which agrees with that found for "ordinary sodium chloride," 1.202791 and 1.202790.

After the work had been abandoned for a time the "apatite sodium chloride" solution was evaporated, ignited, recrystallised two or three times, and the specific gravity again determined (No. 5). Another evaporation, ignition and recrystallisation gave value No. 6, the specific gravity of "ordinary sodium chloride" being determined at the same time.

The slight difference between the first and the last determinations for "ordinary sodium chloride" may be accounted for by

a new setting of the thermostat regulator. The measurements taken at the same time under identical conditions are in good agreement. Thus the average for "ordinary sodium chloride" under the earlier conditions agrees precisely with the value for the purest "apatite sodium chloride" (No. 4), while the later value, 1.202867, for "ordinary sodium chloride" agrees closely with the average, 1.202855, of the later values for the still further purified "apatite sodium chloride."

A sample was then taken from each of the two solutions by means of the pycnometer and ignited to constant weight in platinum, all precautions being observed. When corrected to vacuum the "ordinary sodium chloride" weighed 3.31262, while the "apatite sodium chloride" weighed 3.31267, or 0.05 mg. more, a difference less than the errors of weighing (0.1 mg.). It follows that the atomic weight of the apatite chlorine does not differ from that of ordinary chlorine by an appreciable amount. Even if the solubilities found (26.357 per cent at 18° or 35.790 g. per 100 g. of water) were not absolutely correct, the atomic weight 35.46 calculated from the relative values would still hold good.

Incidentally, we have compared the solubilities we found with those calculated from the formula of Andreae<sup>3</sup> which are in good agreement with many recent determinations.<sup>4</sup> The calculated value is 26.363 per cent., while we found 26.357 per cent., which is in excellent agreement.

#### SUMMARY.

The chlorine isotopes in Bamle apatite occur in the same proportion as in ordinary sodium chloride.

*Christiania, Norway.*

(From the "Journal of the American Chemical Society," July, 1923, 1577-1579).  
[Contribution from the Chemical Laboratory of the University of Wisconsin.]

<sup>3</sup> Andreae, *J. prakt. Chem.*, 1884, XXIX., 467.

<sup>4</sup> Taylor, *J. Phys. Chem.*, 1896-1897, I., 718. Berkeley, *Phil. Trans.*, 1904, CCIII., 189. Fontein, *Z. physik. Chem.*, 1910, LXXIII., 212. Cohen, *ibid.*, 1912, LXXV. Schreinemakers, *Arch. Neer. sci. nat.*, XV.

## THE ACTION OF SELENIUM OXYCHLORIDE ON PURE RUBBER.<sup>1</sup>

By CARL E. FRICK.

In the studies on the oxychloride of selenium which have been in progress in this Laboratory, Lenher<sup>2</sup> has shown that pure rubber, vulcanised rubber, and vulcanite, react chemically with selenium oxychloride. It seemed advisable to undertake a quantitative study of this reaction, if possible, as any information would be interesting in view of our incomplete knowledge of the nature of the rubber hydrocarbon. The products obtained by the action of selenium oxychloride on 2 wild, and 2 plantation rubbers, and a synthetic rubber prepared from isoprene, were investigated.

### PREPARATION OF MATERIALS.

*Selenium Oxychloride.*—The method of Lenher<sup>3</sup> was used.

*Pure Rubber Hydrocarbon.*—Samples<sup>4</sup> of crude, unworked rubber were washed in frequent changes of water until dirt and soluble impurities were removed, dried, and freed from resins by extraction with boiling acetone for 24 hours. The residue was freed from acetone and the rubber hydrocarbon dissolved in pure carbon tetrachloride. The undissolved protein was filtered off and the rubber precipitated by absolute alcohol. The sample was freed from alcohol, redissolved in carbon tetrachloride, reprecipitated by alcohol 7 times, and finally redissolved and kept in pure carbon tetrachloride. The following natural rubbers were used in this study: Upriver, fine, hard Para; first latex Pale Crepe; Upper Caucho Ball; and ribbed Smoked Sheet.

*Synthetic "Isoprene Rubber."*—This was prepared from pure isoprene by the well-known method discovered practically simultaneously by Mathews<sup>5</sup> in England

and Harries<sup>6</sup> in Germany, using metallic sodium to effect the polymerisation. The rubbery mass was washed with acetone, dissolved in carbon tetrachloride, reprecipitated by alcohol, redissolved and reprecipitated several times, and thus purified in exactly the same manner as the natural rubbers. The sample was finally redissolved and kept in pure carbon tetrachloride.

*Isoprene.*—The isoprene was prepared from *dl*-limonene (dipentene) by passing the vapours over an electrically-heated platinum wire, using the principle of Harries' isoprene lamp.<sup>7</sup> The limonene was obtained from washed orange oil, which was over 96 per cent. pure limonene. The crude isoprene was free from any contained amylene by allowing it to stand for several days in contact with barium dioxide, dried with fused calcium chloride and distilled, then dried with metallic sodium and redistilled, using a Vigreux fractionation column. Ostromuislinskii's<sup>8</sup> method of purification by forming the tetrabromide and then removing the bromine by treatment with zinc dust at 0° in absolute alcohol solution was found to be impractical when it was desirable to prepare a litre or more of pure isoprene. The material was colourless; b.p., 33.2-33.8° (742 mm.).

*Solvents.*—Acetone was freshly distilled over anhydrous potassium carbonate, and the fraction boiling at 56-57° used. Carbon tetrachloride was purified by treatment with saturated chlorine water for several days in diffused sunlight. It was then washed thoroughly with distilled water, dried over fused calcium chloride and distilled.

### EXPERIMENTAL PART.

When crude rubber, vulcanised rubber, or even vulcanite is placed in selenium oxychloride, a vigorous reaction sets in, and the rubber is dissolved with evolution of heat. The solution becomes reddish brown in colour and contains selenium monochloride and selenium, in addition to the decomposition products of the rubber. In order to study this reaction, it became evident at once that the reaction would have to be more carefully controlled, and further that

<sup>1</sup> This paper is constructed from a part of a thesis submitted by the author to the Graduate School of the University of Wisconsin in partial fulfilment of the requirements for the degree of Doctor of Philosophy, January, 1923.

<sup>2</sup> Lenher, *Jour. Amer. Chem. Soc.*, 1921, XLIII., 29.

<sup>3</sup> Lenher, *ibid.*, 1920, XLII., 2498.

<sup>4</sup> These samples were kindly furnished by Dr. W. C. Geer, of the B.F. Goodrich Co., and Prof. H. E. Simmons, of the University of Akron.

<sup>5</sup> Mathews and Strange, *Brit. pat.* 24,790, 1912.

<sup>6</sup> Harries, *Ann.*, 1911, CCCLXXXIII., 157.

<sup>7</sup> Harries and Gottlob, *Ann.*, CCCLXXXIII., 228.

<sup>8</sup> Ostromuislinskii, *J. Russ. Phys. Chem. Soc.*, 1916, XLVII., 1983.

the results would be the easier to interpret, the purer the samples of rubber used. The reactions of selenium oxychloride on the purified rubber hydrocarbon in solution in carbon tetrachloride, were carried out in all cases as follows.

To a known quantity of a 5 per cent. solution by weight of pure rubber in dry carbon tetrachloride, cooled to 0°, was added slowly, with vigorous stirring, an excess of a 5 per cent. solution of selenium oxychloride in dry carbon tetrachloride, also cooled to 0°. The selenium oxychloride was added in slight excess as otherwise the solution could not be filtered because the excess of rubber clogs the filter. A yellowish-white, amorphous substance immediately settled. The solution was filtered quickly through a Büchner funnel, the precipitated material transferred to a beaker containing cold carbon tetrachloride and agitated in order to

free the material from the slight excess of selenium oxychloride. This operation was repeated several times, using fresh portions of cold, dry carbon tetrachloride. The precipitated material was finally brought on to the filter paper and the carbon tetrachloride replaced by ethyl ether. The ether was quickly evaporated, the dry, amorphous powder transferred to a glass-stoppered weighing bottle and this container kept at 0°. Due to its instability at ordinary room temperatures and the consequent evolution of hydrogen chloride, the material had to be handled in this way. This instability also prevented further purification of the material by any of the usual methods.

Table I. shows the comparative results based on the averages of all of the complete analyses of the various reaction products of selenium oxychloride with the natural rubbers and the synthetic isoprene

TABLE I.

AVERAGE ANALYSES<sup>9</sup> OF THE PRODUCTS OF THE REACTION BETWEEN RUBBER AND SELENIUM OXYCHLORIDE

SeOCl <sub>2</sub> reaction products with	C %	H %	Se %	Cl %	(Diff.) %	Ratio C:H
"Isoprene Rubber" .....	23.72	4.67	22.57	23.79	25.25	10:23.3
Pale Crepe .....	23.75	4.37	22.81	24.23	24.84	10:22.3
Smoked Sheet .....	21.60	4.66	27.04	24.69	22.01	10:26.0
Para .....	23.85	4.42	26.74	26.03	18.96	10:22.1
Caucho Ball .....	24.49	4.37	26.09	25.35	19.70	10:21.1

## DISCUSSION.

Attention is called to several points brought out in this table. (1) It will be noted that the average content of carbon in the various reaction products of either synthetic rubber from isoprene, or the natural rubbers, varies less than 1 per cent., except in the case of the product from Smoked Sheet, which is about 2 per cent. lower. (2) The average contents of hydrogen in the various reaction products vary less than 0.4 of 1 per cent. (3) The average content of selenium in the synthetic isoprene-rubber product is practically the same as in the plantation Pale Crepe product. The amount of selenium in reaction products of the other 3 natural rubbers, varies only within 1 per

cent., but all are 4 to 5 per cent. higher than in the case of the Pale Crepe or the synthetic isoprene rubber. It will be noted, however, that the products from all 3 of the natural rubbers in which the latex was coagulated by smoke have a selenium content of 26 to 27 per cent. The Smoked Sheet comes from exactly the same source as the Pale Crepe (cultivated *Hevea brasiliensis*), but the latex of Pale Crepe is coagulated by acetic acid, while the latex of Smoked Sheet is only partially coagulated by acetic acid and is then smoked to complete the process. Possibly this difference in the selenium content of the 2 reaction products can be attributed to the method of coagulation. (4) The average content of chlorine in the various reaction products from either the synthetic or the natural rubber varies about 2.2 per cent. (5) The ratio of carbon to hydrogen has changed from C<sub>10</sub>H<sub>16</sub> in the pure rubber, up to C<sub>10</sub>H<sub>26</sub> in the reaction products. (6) Parallel with the chemical changes in the various kinds of rubber upon treatment with selenium moxychloride, there

<sup>9</sup> The "average analyses" are the means of the results of 10 to 12 determinations on different samples of the same material handled under as nearly the same conditions as possible. The average analysis for each constituent is accurate to at least 1 per cent.

is a great change in their physical properties. The products are all amorphous powders, having lost their elasticity and swelling power, and are insoluble in the ordinary rubber solvents, such as benzene, carbon tetrachloride, chloroform and ether. (7) The two most important conclusions that can be drawn from the comparative data on these reaction products are: (a) the pure rubber hydrocarbon from natural *Hevea* rubbers, shows a slightly different behaviour in its reaction with selenium oxychloride, depending upon the source of the rubber and its method of coagulation; (b) judging by the behaviour towards selenium oxychloride, there is no difference in empirical composition between the pure rubber from a typical natural rubber, such as Pale Crepe, and a synthetic rubber, made by the polymerisation of isoprene by metallic sodium. This statement is in contradiction to the recent article of Kirchof.<sup>10</sup> Kirchof has compared the ultimate analyses that have been made on the rubber hydrocarbon from different sources and also the analyses of the various derivatives that have been reported. He concluded that synthetic rubber is a true polymer of the corresponding hydrocarbon,  $C_5H_8$ , but that the hydrocarbon of Para rubber has the empirical composition  $C_{10}H_{17}$ , and cannot be formed from the hydrocarbon  $C_5H_8$  through polymerisation, as Harries supposed. According to Kirchof, neither the empirical composition nor the structure of synthetic rubber is identical with that of Para rubber.

The present work tends to support the conclusion that Harries reached after a study of the hydrolysis products of the ozonides of various kinds of natural and synthetic rubbers, namely, that there is no essential difference in constitution between natural rubber and the polymerised isoprene.

The author wishes to express his appreciation to Professor Victor Lenher, at whose suggestion and under whose direction this work was carried out; also to Professor Homer Adkins for helpful suggestions.

#### SUMMARY.

1. The reactions between selenium oxychloride and the natural, *Hevea* rubbers, Pale Crepe, Smoked Sheet, Para and Caucho Ball, have been studied.

2. The reaction between selenium oxychloride and a synthetic rubber made by polymerising isoprene has been studied.

3. It has been found that when the various rubbers are treated with selenium oxychloride their physical properties are changed. The products are all amorphous powders, having lost their elasticity and swelling power, and are insoluble in the ordinary solvents for rubber.

4. It has been shown that the pure rubber hydrocarbon from natural, *Hevea* rubbers, shows a slightly different behaviour in its reaction with selenium oxychloride, depending upon the source of the rubber and its method of coagulation.

5. It has been shown definitely that, judging by their respective behaviours towards selenium oxychloride, there is no difference in empirical composition between the pure rubber hydrocarbon from the *Hevea* tree and the synthetic rubber made by polymerising isoprene with metallic sodium.

Madison, Wisconsin.

(From the "Journal of the American Chemical Society," July, 1923, 1800-1804).

#### SOCIETY OF GLASS TECHNOLOGY.

In connection with the visit of members of the Society of Glass Technology to France, during the first week of July, two meetings with French glass manufacturers were held on Monday July 2. In the morning, the visiting party was received by the Chambre Syndicale des Maitres Verreries, and was welcomed by its President, Mons. L. Houdaille, who described to the visitors how the French glass manufacturers were all united in one body—the Chambre Syndicale—which was divided into six sections representing various branches of the industry. The work of these sections was organised in such a way as to prevent ruinous competition between members, and at the same time encouraged individual research and development. Mons. L. Delloye spoke of the need for co-operation among manufacturers of different countries. Prof. W. E. S. Turner, Col. S. C. Halse and Mr. E. A. Hailwood replied for the Society of Glass Technology.

In the afternoon (after a lunch at which visiting members were the guests of the

<sup>10</sup> Kirchof, *Kolloidchem. Beihefte*, 1922, XVI., 47.

Chambre Syndicale des Maitres Verreries), a joint meeting of the Société des Ingénieurs Civils and the Society of Glass Technology was held. In the absence of Mons. Guillet, President of the Société des Ingénieurs Civils, Mons. L. Delloye welcomed the visitors. The following papers were communicated:—

PROF. H. LE CHATELIER, *La Méthode Scientifique dans l'Industrie.*

DR. A. GRANGER, *Les Verres Opaques et Colorés, et les Glacures Céramiques de Même Espèce.*

MONS. LAFON, *La Dilatation des Verres et Cristaux.*

PROF. W. E. S. TURNER, *Specifications for Glass Products.*

MR. T. TEISEN, *Improvements in the Design of Recuperative Glass Pot Furnaces.*

MR. S. ENGLISH and PROF. W. E. S. TURNER, *The Physical Properties of Boric Oxide Glasses.*

During the week-end visits were paid to the following glass works: (a) Etablissements Legras at St. Denis, (b) Verreries de Reims (Messrs. Charbonneaux & Cie), (c) New plate glass works at Chantreine, (d) Glaceries de St. Gobain, Chauny and Cirey. Members took the opportunity when at Reims of visiting the battlefields in that district. A visit was also paid to the sand quarries at Nemours, and to the Forest and Castle of Fontainebleau.

The social side of the excursion was not neglected. In addition to the reception and lunch already mentioned, a complimentary dinner was given by members of the visiting party to Mons. L. Delloye, who had been responsible for making all the arrangements on the French side. At Noyon the party was kindly invited to lunch by the directors of Les Glaceries de St. Gobain, Chauny and Cirey. A reception was also given to visitors by Mons. G. Despret (Administrateur des Verreries de Boussois), Paris, when an interesting exhibition of artistic glass was on view.

Altogether, some thirty British members of the Society and their friends took part in the visit. It will be recalled that a party of members of the Society visited America in 1920. Encouraged by the success of both these visits it is proposed to arrange other tours as opportunity arises.

## THE INSTITUTE OF CHEMISTRY OF GREAT BRITAIN AND IRELAND.

JULY EXAMINATIONS: 1923.—PASS LIST.

The following candidates have passed the examination for the Associateship:—

*In General Chemistry:* Anderson, Alex Carr, B.Sc. (Lond.), University College, Nottingham; Barnett, John, East London College; Beard, Herbert Greensmith, Huddersfield Technical College; Bennett, William Frederick, Central Technical School, Liverpool; Booth, Walter, Central Technical School, Leeds; Bott, Thomas Harold, B.Sc. (Lond.), College of Technology, Manchester; Bubb, Frederick James, B.Sc. (Lond.), East London College; Child, Reginald, King's College, London; Crombie, William, Imperial College of Science and Technology; Crutchlow, Bernard William Alfred, King's College, London; Curtis, Ronald Hamilton, University College, London; Faichney, Peter, Heriot-Watt College, Edinburgh; Fairgrieve, Adam Wilson, Heriot-Watt College, Edinburgh; Groves, Adam Traill, Heriot-Watt College, Edinburgh; Harrow, Andrew Nicoll, Heriot-Watt College, Edinburgh; Hibbert, Sydney, A.M.C.T., College of Technology, Manchester; Hill, Herbert Eric, University of Western Australia; Jones, Norman Ellathorne, King's College, London; Kimmins, Lionel George, B.Sc. (Lond.), University College, London; Kirby, Christopher Stanhope, University College, London; Laing, William Mossman, Heriot-Watt College, Edinburgh; Leaper, Percy Joshua, University College, Southampton; Lindsay, Robert, University College, London; McGrath, James, Royal Technical College, Glasgow; Mieras, Adrian Pieter, Heriot-Watt College, Edinburgh; Mosley, Martin Aaron, University College, Nottingham; Moyes, Robert Baird, Heriot-Watt College, Edinburgh; Oliver, James Herbert, B.Sc. (Lond.); Paul, David, Heriot-Watt College, Edinburgh; Pound, Albert, B.Sc. (Lond.), University College, Exeter; Rosewarne, Joel Alfred Henry Tetterdell, King's College, London; Russell, William Lyle, Heriot-Watt College, Edinburgh; Saunders, Harold Nicholas, B.Sc. (Lond.), University College, Exeter; Scott, Robert, Heriot-Watt College, Edinburgh; Smith, Charles George, King's College, London; Snelus, Miss Suzanne Mabel Lavinia, College of Technology, Manchester, and Sir John Cass Technical Institute; Thacker, Gilbert Doe Dwyer

Way, East London College; Thomas, Brynmor, M.Sc. (Dun.), Central Technical School, Liverpool; Threadgold, Herbert, B.Sc. (Lond.), University College, London; Tully, James Duncan, B.Sc. (Lond.), University College, Southampton; Walker, John, Technical College, Huddersfield; Wells, William Herbert, University College, London; Wilkie, Alexander Stewart, Heriot-Watt College, Edinburgh; Wilson, George Edward, Heriot-Watt College, Edinburgh; Wood, Thomas, Central Technical School, Liverpool; Wylie, Andrew Robertson, Heriot-Watt College, Edinburgh. (28 candidates failed to satisfy the examiners.)

*In Branch (b): Metallurgical Chemistry:* Howard, Thomas George, Sir John Cass Technical Institute.

*In Branch (e): Chemistry, including Microscopy, of Food and Drugs, and Water:* Woodhead, John Ezra, B.Sc. (Lond.), Birkbeck College, and Northern Polytechnic Institute, London.

*In Branch (g): Chemical Technology:* Martin, George Frank, Royal College of Science, London.

The following Associates have passed the examination for the Fellowship:—

*In Branch A: Inorganic Chemistry:*

Hackney, Norman, B.Sc. (Lond.); Wynn, William Owen Roderick.

*In Branch C: Organic Chemistry:* Cohen, Abraham, B.Sc. (Lond.).

*In Branch D: Agricultural Chemistry:* Ritchie, John Edwin, M.A., B.Sc. (Aberd.).  
By Order of the Council,

RICHARD B. PILCHER,  
*Registrar and Secretary.*

30, Russell Square, London, W.C.1.  
June 27, 1923.

#### PRESENTATION OF THE SOCIETY'S ALBERT MEDAL TO SIR DAVID BRUCE AND SIR RONALD ROSS.

The Council of the Royal Society of Arts attended at Clarence House, St. James's, on July 13, when His Royal Highness, the Duke of Connaught and Strathearn, K.G., President of the Society, presented the Society's Albert Medal for the present year in duplicate to Major-General Sir David Bruce, K.C.B., D.Sc., LL.D., F.R.C.P.,

F.R.S., and Colonel Sir Ronald Ross, K.C.B., K.C.M.G., D.Sc., LL.D., M.D., F.R.C.S., F.R.S., "in recognition of the eminent services they have rendered to the Economic Development of the World by their achievements in Biological Research and the Study of Tropical Diseases."

The Duke of Connaught was attended by Lieut.-Colonel Sir Malcolm Murray, K.C.V.O., C.B., C.I.E.

#### A PEROXIDE ELECTRIC CELL.

By A. E. J. PETTET & A. W. WARRINGTON.

The writers apologise if the cell they are about to describe is not new.

The elements and pots of an ordinary Bunsen cell are used. The zinc is amalgamated and placed in the outer cell, containing a solution of zinc sulphate (144 gm. of the crystallised salt per litre). The carbon is placed in the porous jar and is in contact with a "20" volume solution of hydrogen peroxide, acidified with sulphuric acid (one volume of acid to every ten volumes of the peroxide.).

The cell very rapidly reaches its full strength. Its E.M.F. is about 1.6 volts. The internal resistance of the cell used by the writers was about 1 ohm. (The outer cell had a liquid capacity of about 480 c.c., and the inner cell of about 210 c.c.) The cell is very clean to work with, and for renewal only the contents of the inner compartment need be replenished. It may be left for about a week on open circuit without appreciable deterioration.

The cell is very constant. With a current of 0.06 ampere it will run for 48 hours unchanged, and for another 24 hours with only a slight fall in current. If used continuously it has a total output of about 26,500 (25,000) coulombs. It runs down quite rapidly at the end of about three days, owing to decomposition of the peroxide. It worked well, however, until only about one-twentieth of the original amount of available oxygen was present.

It is admirably adapted for use with a copper voltameter. Running for one hour through a copper voltameter, and carrying a mean current of 0.2082 ampere, the highest reading of the galvanometer, the needle of which was suspended by a silk fibre, indicated a current of 0.2185, and the lowest of 0.2019 ampere. Running for two hours through a copper voltameter, and carrying a mean current of 0.0990 ampere,

the current varied between 0.0998 and 0.986. With a current of 0.06 ampere it will run continuously for two or three days, as already stated, with almost inappreciable change in current strength.

The writers have no hesitation in recommending its use in schools in place of the Daniell cell.

#### ARTIFICIAL SILK.

*Canadian Chemistry and Metallurgy, July, 1923.*

Artificial silk is the rather inappropriate name given to a product of cotton or wood fibre which differs both physically and chemically from the gum of the silk worm. So long as it is called "artificial" a certain prejudice against its use is bound to exist, as was the case with cotton in its early days when it was looked upon as a substitute for linen. Cellulose silk—a more fitting term—is a commodity in a class of its own, and of indisputable value. The world's present output, though nearly twice that of pre-war days, is far from sufficient to meet the demand, and the industry, wherever carried on, is enjoying a prosperity that suffered no interruption even in the 1921 period of general business depression. The great artificial silk firm of England, Courtaulds, Limited, reported a net profit for 1922 of £3,018,431, which compares with £1,684,593 in 1921 and £1,804,796 in 1920.

Of the four processes in common use for the making of cellulose silk, the most popular is the viscose, which is an entirely British discovery, depending upon the formation of a soluble xanthate compound. The raw material for this process is wood pulp, and the principal chemical reagents caustic soda and carbon bisulphide. The viscose factories in Europe draw their supplies of sulphite pulp from Scandinavia and Canada. It is the labour, however, not the raw material, that constitutes the heaviest item of cost; but this will not be so much in evidence when the present machinery is improved and additional mechanism applied.

The possibilities of cellulose silk appear to be almost limitless. It is extensively used in the braiding and millinery industries; and, woven with real silk, wool, cotton or other fibres, it is gaining in importance every day in the manufacture of wearing apparel and of beautiful textures of all kinds. Ribbon straw, artificial horsehair, cloth, and even imitation Smyrna rugs and

Gobelin tapestries are now made in artificial silk plants. Though not a substitute for natural silk, cellulose silk has a broad market on account of its comparative cheapness, and the world's output will soon exceed that of cocoon silk. The chemistry of cellulose offers unlimited scope for research, so new developments can be looked forward to that will still further extend the use of cellulose silk.

In view of the Finance Minister's tariff recommendations and the trading advantages Canada has with some countries through her preferential tariffs, the time would appear to be opportune for examining fully into the feasibility of establishing the cellulose silk chemical industry in Canada. Sulphite pulp and the necessary chemicals can be manufactured cheaply, and our domestic market is not insignificant, as statistics for 1922 reveal that over \$2,000,000 was expended on imports of cellulose-silk yarn and filaments, about \$1,000,000 on manufactures from the United States and the United Kingdom alone, and large quantities—not to be identified in trade figures—of fabrics from these and other countries.

Just as we go to press we learn that the large British firm of Courtaulds has decided to establish a plant near Quebec City for the manufacture of artificial silk yarn. Truly we are getting on.

#### NOTICES OF BOOKS.

*Organic Chemistry*, by IRA REMSEN, Revised and Enlarged by W. R. ORNDORFF. Pp. XI. + 567. London: Macmillan & Co., Ltd., St. Martin Street, W.C.2. 1923. 10s. net.

Prof. Remsen's textbooks possess the admirable quality from the teaching standpoint, of being simple and containing a minimum of descriptive matter.

This volume on Organic Chemistry is not over-burdened with the modes of preparation and the properties of countless compounds. Indeed, in this edition, revised with the help of Prof. Orndorff, the practical directions for preparing even important substances has been omitted. This is not, however, a serious drawback, since it allows more attention to be devoted to principles and generalisations. Further, it is now customary to use laboratory manuals in connection with practical organic chemistry.

The judicious introduction of new discoveries and developments has been ably

done, and very few errors — and these are trivial—have been noticed.

This new and enlarged edition is well adapted for the use of students attending an introductory course of Organic Chemistry, and should commend itself to lecturers in the subject.

#### CHEMICAL SOCIETY'S LIBRARY.

Owing to the work of redecorating the rooms of the Society, the Library will be closed during the entire month of August, and in accordance with the usual practice will close at 5 p.m. daily from September 1 to 17.

#### NOTES.

Messrs. Longmans, Green & Co. announce that the new edition of Sir Edward Thorpe's *Dictionary of Applied Chemistry* will extend to seven volumes, a great part of the last volume being devoted to a complete index to the work.

#### BOOKS RECEIVED.

*Etude sur la Tannerie et les Industries connexes au Març*, Ch. ZIEGLER INGENIEUR CHIMISTE. Pp. 122. 1923. La Chaussiere Francaise, 141, Boulevard Sebastopol, Paris. 7fr. 50c.

*The Ventilation of Public Buildings*, by ROBERT BOYLE. Pp. LI. + V. 1923. Messrs. Robert Boyle & Son, 64, Holborn Viaduct, E.C.1. 6s. net.

The Publications Department, Bournville, has issued two pamphlets by A. W. KNAPP, B.Sc., F.I.C., entitled *The Application of Science to Cacao Production*, and *The Separation and Uses of Cacao Shell*, price 6d. each.

The articles were originally prepared for the International Congress of Tropical Agriculture, and appeared originally in the *Journal of the Society of Chemical Industry*, but have been revised and brought up-to-date.

Both are interesting and informative, and are written in a way suitable for those who are not specialists in this particular subject.

The U.S. Department of the Interior, Bureau of Mines, has issued the following bulletins:—

No. 204. *Underground Ventilation at Butte*, by DANIEL HARRINGTON. Pp. 31.

No. 339. *Coal-Mine Fatalities in the United States, 1922*, by WM. W. ADAMS. Pp. VI., 97.

No. 340. *Production of Explosives in the United States during the Calendar Year 1922*, by WILLIAM W. ADAMS. Pp. 25.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 18008—Bloxam, A. G.—Manufacture of azo dyestuffs. July 11.  
 18087—Bodrero, B.—Production and use of sulphuro-phosphate. July 12.  
 18061—Dreyfus, H.—Treatment of cellulose derivatives. July 12.  
 18092—Farbwerke vorm. Meister, Lucius, and Bruning.—Manufacture of highly-active charcoal. July 12.  
 17764—Lilienfeld, L.—Manufacture of cellulose ethers. July 9.  
 17808—Moeller, J. F. L.—Method of treating carbonaceous materials. July 10.  
 17837—Moeller, J. F. L.—Fractional distillation of hydrocarbons. July 10.  
 18107—Trumble, M. J.—Treating hydrocarbons. July 12.  
 18250—Vogel, H.—Manufacture of colloidal sulphur. July 14.

#### Specifications Published this Week.

- 199750—Joyner, R. A., and Nobel's Explosive Co., Ltd.—Manufacture of hydrazine.  
 166759—Hirschberg, L. M.—Manufacture of aqueous solutions of formaldehyde.  
 199760—Hirschberg, L. M.—Production of formaldehyde by catalysis.  
 199766—Hanna, R. W.—Process for the continuous production of low boiling-point hydrocarbons from petroleum oils.  
 199870—Farbwerke vorm. Meister, Lucius, and Bruning.—Manufacture of therapeutically active acridine derivatives.  
 188335—Appareils et Evaporateurs Kestner.—Process of extracting sodium bicarbonate and other salts contained in natural soda bicarbonated mineral waters.

#### Abstract Published this Week.

- 197848—Thymol.—Howard & Sons, Ltd., Uphall Works, Ilford, and J. Blagden, Apple Tree House, Grove Road, South Woodford, both in Essex.

*Thymol, thymol sulphonic acids, m-cresol sulphonic acids.*—Thymol is prepared by sulphonating *m*-cresol under conditions suitable for producing a polysulphonic acid, such as the di- or even tri-sulphonic acid, which is then condensed with isopropyl alcohol, the sulphonic groups split off and the thymol steam-distilled. According to an example *m*-cresol is treated with oleum, containing 88 per cent. total sulphur trioxide, first at 100° and then at 150° C. A solution of isopropyl alcohol in sulphuric acid is run in and the mixture maintained at 80-90° C. for several hours. It is then heated to 130° C. and a current of steam passed in, the thymol distilling off. A small quantity of by-product may be removed by solution of the thymol in alkali. A little isomeric thymol, melting at 114° C., is also formed.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

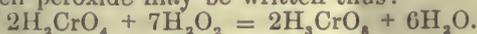
VOL. CXXVII. No. 3304.

## PERCHROMIC ACID.

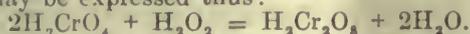
By GEOFFREY N. RIDLEY.

### I.—FORMULÆ.

Perchromic acid has been given two formulæ— $\text{HCrO}_5$  and  $\text{H}_3\text{CrO}_4$ . It therefore deviates from the path followed by its "relative," permanganic acid, whose formula is given as  $\text{HMnO}_4$  or  $\text{H}_2\text{Mn}_2\text{O}_8$ . The equation representing the formation of the acid by the interaction of chromic acid and hydrogen peroxide may be written thus:



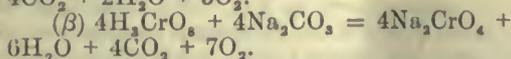
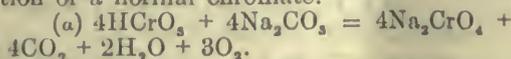
This reaction occurs when the hydrogen peroxide is in excess. Otherwise, acid corresponding to the probable formula  $\text{HCrO}_5$  is produced. In the hypothetical case of the formula for perchromic acid being  $\text{H}_2\text{Cr}_2\text{O}_8$ , the formation of the compound may be expressed thus:



It has been suggested that chromium may form an octovalent compound, perchromic acid consisting of a combination of  $\text{Cr}_2\text{O}_7$  with  $\text{H}_2\text{O}_2$ , or  $\text{CrO}_4$  with  $\text{H}_2\text{O}$ .

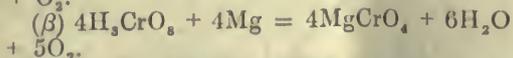
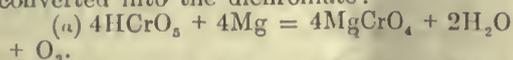
### II.—CHEMICAL BEHAVIOUR.

The ethereal solution of perchromic acid reacts with an alkaline carbonate, such as sodium carbonate, resulting in the production of a normal chromate.



A *perchromate* of sodium does not appear to be formed by the direct reaction between carbonate and acid, but a sodium perchromate,  $\text{Na}_4\text{Cr}_2\text{O}_{18} \cdot 28\text{H}_2\text{O}$ , may be prepared by adding  $\text{Na}_2\text{O}_2$  to an aqueous paste of  $\text{Cr}(\text{OH})_3$ .

The solution of perchromic acid has an acid reaction towards litmus, and acts upon magnesium with appreciable vigour. The metal becomes coated with a deposit of magnesium chromate, portions of which are converted into the dichromate:



Perchromic acid is without action upon

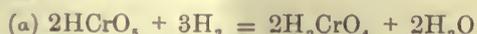
copper. Chemical activity between the acid and phosphorus is not visible, but on warming and allowing the ether to slowly evaporate, a greenish substance is left, which, in view of its chemical behaviour, is thought to be a phosphide of chromium.

### III.—DECOMPOSITION.

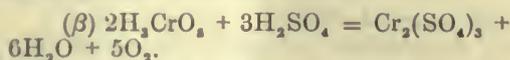
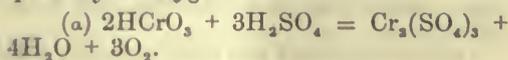
Perchromic acid undergoes decomposition by:

- (a) Nascent hydrogen.
- (b) Acids.
- (c) Compounds, viz., carbonates.
- (d) Metals, viz., magnesium.
- (e) Water.
- (f) Rise in temperature.

The reduction by hydrogen is expressed thus:

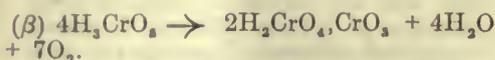


The addition of strong sulphuric acid to perchromic acid brings about the rapid dissolution of the blue compound, accompanied by the evolution of a considerable quantity of oxygen:



As regards the decomposition of perchromic acid by water, the action is slow and only brought about in a short space of time by much shaking. The acid is gradually removed from the ether colouring the water a pale purple, which readily changes to a brownish-red, whence it is concluded that either dichromic or chromic acid is in solution.

If a small quantity of acetone is added to the ethereal solution of perchromic acid, the fluid may be heated gently to a temperature neighbouring on  $50^\circ\text{C}$ . The blue colour of the liquid gradually changes through grey to purple and to dark reddish-brown. This is, in all probability, dichromic acid, and its formation may be expressed thus:



What may be called the "conditions of preservation" of perchromic acid constitute important determining factors in connection with the decomposition of the compound. The conditions of preservation are: Low temperature and in a free state; ordi-

nary temperature and in solution; ordinary temperature and free; elevated temperature and in solution, the solvent being ether.

#### Condition of Preservation.

Low temperature.

Free state.

Solid.

Ordinary temperature.

In solution.

Ordinary temperature.

Free state.

High temperature.

In solution.

The general remark is: that perchromic acid, when in solution, owes its stability to the solvent; when free, to the temperature.

#### IV.—ISOLATION.

The following remarks with regard to the crystallising of perchromic acid may be of interest.

Perchromic acid has been isolated; briefly the process is this:

A solution of chromium trioxide in methyl ether at  $-30^{\circ}\text{C}$ . is treated with 97 per cent. hydrogen peroxide solution. The blue crystals formed are said to be those of perchromic acid.

The relation between these conditions and the dissolution of perchromic acid is shown in the table.

Remarks on Decomposition.	
Temperature.	Speed.
$-20^{\circ}\text{C}$ .	
to	Rapid.
$-25^{\circ}\text{C}$ .	
Ordinary temp.	Very slow. (Several hours.)
Ordinary temp.	Immediate.
$35^{\circ}\text{C}$ .	
to	Gradual.
$50^{\circ}\text{C}$ .	

If, on the other hand, a frozen solution of potassium dichromate at  $-12^{\circ}\text{C}$ . be treated with conveniently cooled and acidulated hydrogen peroxide, the superincumbent ether assumes a deep blue colour. The temperature being low, all remains solid, allowing the blue ethereal solution to be poured off. At a temperature between  $-20^{\circ}$  and  $-25^{\circ}\text{C}$ . this liquid deposits blue crystals, which melt very rapidly when removed from the freezing bath.

This experiment was carried out by the writer previous to receiving information concerning the method by which perchromic acid was isolated in 1914.

## ORGANIC COMPOUNDS OF ARSENIC.

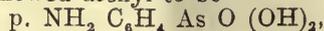
### PART II.

By R. F. HUNTER, F.C.S.

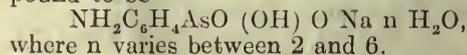
In Part I. some account was given of atoxyl in general terms, and it is now proposed to treat the matter more thoroughly.

#### ATOXYL.

Owing to theoretical considerations current among the French school of chemists of Béchamp's time, Béchamp was prevented from arriving at the correct conclusion for his reaction, and further, the chemists of his day refused to regard his compound obtained from arsenic acid and aniline as a true organic arsenic compound, and, as stated in Part I., not until the work of Ehrlich, to whom we owe the discovery of our present most efficient cure for syphilis, appeared in the year 1907, was the true nature of Béchamp's compound demonstrated. Ehrlich and his co-worker Berthelm showed atoxyl to be



and further, the commercial sodium compound to be



Researchers in this field following Ehrlich, applied the Béchamp reaction to other aromatic amines with a free para. position, this led to the discovery of 2-aminotolyl-5-arsenic acid from o-toluidine.

As stated before, the main trouble involved in the use of atoxyl for injections is its toxic nature; acetylation in the case of such compounds as aniline had yielded the less toxic acetanilide. Consequently atoxyl was acetylated, and a drug of constitution,  $\text{CH}_3\text{C(O)NH C}_6\text{H}_4\text{AsO(OH)ONa} \cdot n\text{H}_2\text{O}$ , was introduced.

It is necessary to examine systematically the derivatives of atoxyl, and I propose to again use Gibson's method of classification.

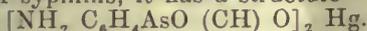
Gibson, in his recent work: *Organic compounds of arsenic and antimony*, has divided the atoxyl derivative as follows:—

(1) p-Arsanilic acid and its N-Acyl and Alkyl derivatives. p-Arsanilic acid, Béchamp's compound, is usually prepared by

heating corresponding quantities of aniline and arsenic acid at 180° for some two hours.

$C_6H_5NH_2 + H_3AsO_4 = NH_2C_6H_4AsO(OH)_2 + H_2O$ ,  
the sodium salt is, of course, atoxyl.

Mercuric derivative of p-Arsanilic acid. Sometimes known as "Asyphil," has sometimes been used for injection in the case of syphilis, it has a structure



The important acyl derivative of atoxyl is the acetylone "Arsacelin" which is sodium Acetyl p-arsenilate and has received considerable application.

Some other acyl derivatives are:

Formyl, chloroacetyl, butyryl, malonyl, benzoyl, allylthio carbamino, theo carbamino, methyl carbamino, phenyl carbamino, p-arsanilic acids.

p-Sulphomethyl aminophenylarsinic acid.  $SO_3HCH_2NH_2C_6H_4AsO(OH)_2$  is worthy of note, and is prepared by treating atoxyl with formaldehyde and sodium bisulphite in aqueous solution.

Three other series of compounds belonging to the group are:—

Aldehyde condensation products of atoxyl phenylglycine arsenic acid and homologues and phenylmethyl glycine p-arsenic acid and its c. esters.

(2) Isomerides of p-Arsanilic acid, viz., m-Aminophenylarsenic acid and its derivatives.

(3) Homologues and substitution products of p-Arsenic acid homologues, such as Aminotolylarsenic acids, the 2-aminotolyl-5-arsenic acid is important, and the sodium derivative  $NH_2C_6H_3(CH_3)AsO(OH)ONa$  has found application under the title of "Kharsin."

o-Anisidine-4-arsenic acid is the most common derivative. 2-Acetyl 1:5 benzarsenic acid is an interesting example of an aminobenzarsenic acid.

The halogen derivatives are not important, the thio derivatives are classified under

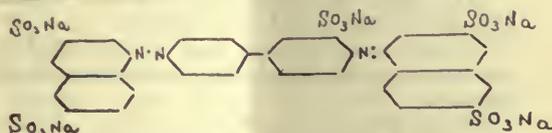
- (a) Disulphides,
- (b) Sesquisulphides,
- (c) Monosulphides.

(4) Homologues and derivatives of o-Arsenic acid 4-aminotolyl-3-arsenic acid is worthy of mention prepared from p-toluidine and  $H_3AsO_4$ .

(5) Nitroso, azo, diazo and triazo phenyl arsenic acids and derivatives.

The azo compounds are of use in medicine since they have a fatal effect on the protozoa of certain diseases, for instance,

trypan red had been used in sleeping sickness, and has a structure,

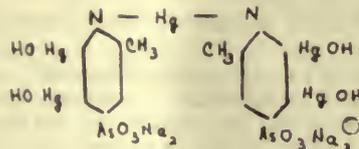


and is prepared by diazotisation of both amino groups in benzidine or the sulphonic acid and coupling with 2-naphthylamine-3:6-disulphonic acid.

(6) Organo mercurial compounds of p-Arsenic acid and derivatives.

From the beneficial results of the use of mercury compounds in the treatment of venereal disease, we should expect a compound of the nature of p-arsenic acid and mercury to be quite a good cure. Consequently it was attempted to combine the therapeutic properties of mercury with those of atoxyl, and the results were beneficial. Condensation of mercury acetate with atoxyl being main reaction, from which were obtained on successive concentration sodium 3:5-dehydroxymercuri-4-aminophenylarsinate.

A new compound tested clinically with poor results is "Hydryl," which has the composition,



(7) 4:4' Diaminodiaryl arsenic acids. These were discovered as a result of applying the Béchamp condensation to aniline and o-toluidine.

4:4' Diaminodiphenylarsenic acid.

$(NH_2C_6H_4)_2AsO(OH)$  is the best example.

(8) Mixed aromatic aliphatic p-amino arsenic acids.

(9) Nitro derivatives of arsenic acids.

Some of these are important:

5-nitro-2-aminophenylarsenic acid.

6-Nitro-m-arsenic acid.

2-nitro-4-aminophenylarsenic acid.

2-nitro-3-aminophenylarsenic acid.

3-nitro-4-aminophenylarsenic acid are worthy of note.

(10) Diaminophenylarsenic acids:

Examples of these are:

2:3 diaminophenylarsenic acid,

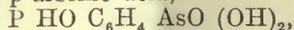


3:4 Diaminophenylarsenic acid are examples.

(11) The Hydronyphenylarsenic acids. Phenol-p-arsenic and homologues.

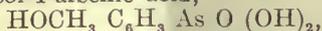
These are of interest and represent the extension of the Béchamp condensation of phenols.

Phenol-p-arsenic acid,



is prepared by heating phenol and arsenic acid in proportions required by theory.

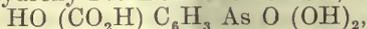
o-Cresol-4-arsenic acid,



in same manner from o-Cresol and corresponding m-compound.

Naphthol-4-arsenic acid,  $\text{HO C}_{10}\text{H}_6\text{AsO (OH)}_2$ , is obtained by adding iced  $\text{NaNO}_2$  solution to 1-aminonaphthyl-4-arsenic acid in 15 per cent.  $\text{H}_2\text{SO}_4$ .

2-Hydroxy-1:5-Benzarsenic acid,



prepared from 2-acetylaminotolyl-5-arsenic acid by oxidation with  $\text{KMnO}_4$  followed by  $\text{NaOH}$  hydrolysis. Its sodium salt is less toxic and is used sometimes in cases of syphilis.

2:4 Dehydroxyphenylarsenic acid.

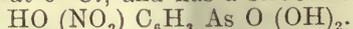
2-Methoxy-4-hydroxyphenylarsenic acid.

2:4-dimethoxyphenylarsenic acid.

3:4-dehydroxyphenylarsenic acid and 4:4-dehydroxydiphenylarsenic acid have also been prepared.

(12) Nitro derivatives of hydroxyphenylarsenic acids.

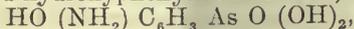
3-nitro-4-hydroxyphenylarsenic acid is produced by nitration of sodium p-Phenol arsenate with a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  at  $0^\circ \text{C}$ ., and has a structure,



4-nitro-2-hydroxyphenylarsenic acid is prepared from diazotisation of 4-nitro-2-aminophenol, followed by warming to decompose diazo salt.

5-nitro-2-hydroxyphenylarsenic acid, 3:5-dinitro-2-hydroxyphenylarsenic acid, and 5-nitro-2:4-dehydroxyphenylarsenic acid have been prepared, and are worthy of mention.

(13) Arsenic acids of amino phenols. 3-amino-4-hydroxyphenylarsenic acid,



is typical and is prepared by reduction of corresponding nitro compound.

3-amino-2-hydroxytolyl-5-arsenic acid, 4-amino-3-hydroxyphenylarsenic acid, carbetoxo, 3-aminophenol-6-arsenic acid. 4-dimethyl amino-2-hydroxyphenylarsenic acid, and 3:5-diamino-4-hydroxyphenylarsenic acid have been described and deserve mention.

## PAN FORMATION IN SOILS IN THE LIGHT OF THE LIESEGANG PHENOMENON.

BY N. G. CHATTERJI, D.Sc., A.I.C.

The formation of pans in soils has been the subject of much investigation, and it may now be taken for granted that the whole process is intimately connected with the colloidal properties of soils. The latest work on the subject has been ably summarised by Morison (*Trans. Farad. Soc.*, 1922, XVII., 2, 321-323), in which the author comes to the conclusion that the whole process is a transformation of soil colloids from the "sol" to the "gel" form with subsequent dehydration and deposition.

Whilst substantially agreeing with the above conclusion, an attempt has been made in the present paper to bring forward evidence showing the similarity between pan formation and that general type of periodic precipitation known as Liesegang phenomenon, after the name of the discoverer. This phenomenon was first observed by the discoverer when doing the following experiment:—

A glass plate was coated with 5 per cent. gelatin solution containing a small amount of potassium chromate. A drop of strong silver nitrate solution was then placed on the gel, and it immediately began to diffuse into the latter. The silver nitrate, of course, reacted with the chromate in the gel, forming the insoluble red silver chromate. But although there was a continuous supply of both the components, the insoluble silver salt was, however, not deposited in a continuous zone round the periphery of the original drop, but in a series of concentric rings, separated by apparently clear zones.

The general conditions observed with the soils in which pans are formed are here given briefly, taken mainly from a paper on the subject by Morison and Sothers (*Journ. Agri. Scien.*, 1914, VI., 84). The pan layer in a soil consists more or less of a well-defined band of material where the gradual transition from the surface to the underground soil is broken. The characteristics of this layer are a large diminution of pore space of the soil cutting off the air and water movement and preventing the penetration of plant roots. The concentration of the soil into such a layer may be of two kinds: it may be caused by the continued passage of heavy instruments of tillage to a given depth, or by the removal of material either

in the form of colloid sols or in the state of solution and its deposition at lower depths in the soil where it acts as the cementing material to the normal soil particles.

The present paper is concerned with the latter kind of pan.

Pan formation of this nature is almost always confined to soils composed for the most part of quartz sand, and as the normal drainage in such soils is rapid, the existence of the impervious layer is very marked. The pan layer, which occurs at a

depth of 5-60 cms., varies in colour from a dark brown to a reddish yellow. The sub-soil appears to be the ordinary and typical sand of the locality, unaltered in any way. The zone immediately above the pan is remarkable in the fact that it is almost free of iron and aluminium, and hence has a bleached appearance. The surface soil is usually rich in acid humus, and is almost completely free from calcium carbonate. The analytical figures for two typical samples of pan-bearing soils are given below:

	Frendenstadt, Swarzwald.		Swarzwald.			
	Bleached sand.	Pan layer.	Subsoil.	Bleached sand.	Pan layer.	Subsoil.
Fe <sub>2</sub> O <sub>3</sub> .....	0.253	1.857	0.906	0.193	0.767	0.552
Al <sub>2</sub> O <sub>3</sub> .....	0.180	4.946	1.268	0.455	2.133	0.975
CaO .....	trace	0.019	0.210	0.031	0.036	0.029
MgO .....	0.015	0.118	0.088	0.011	0.025	0.031

The main facts, therefore, in connection with the presence of pans in soils are the following:

(1) The formation of pans generally in sandy soils of open texture.

(2) A considerable accumulation of organic matter in the surface soil.

(3) Concentration of iron and aluminium hydroxides in the pan layer and other lower layers.

(4) The almost complete absence of calcium carbonate in the surface soil.

Various theories have from time to time been advanced to explain this phenomenon from the chemical point of view, such as the alternate reduction and oxidation of iron humates, but an exhaustive examination of these (Morison and Sothers, *loc. cit.*, Stremme, *Kolloid Zeitsch.*, 1917, XX., 161) shows that the most probable explanation of the phenomenon lies in the colloidal properties of soils.

We have already mentioned the curious phenomenon of banded structure of the precipitate of silver chromate formed by the interaction of silver nitrate solution with potassium chromate in gelatin gel. It has been found that various other media, such as agar-agar and silicic acid gels also behave in the same way as gelatin. But the action of gels in bringing about periodic precipitation is specific. For example, silver chromate forms rings in gelatin, but not in agar-agar, while lead iodide gives these in the latter but not in the former. We have observed that ferric hydroxide gets precipitated in rings when a soluble ferric salt is present in silicic acid gel, and gets slowly

acted upon by an alkali from above. Recently, Bhatnagar and Mathur (*Kolloid Zeit.*, 1922, XXX., 368-71) have been successful in preparing a number of different kinds of periodic precipitates in this gel.

No satisfactory explanation has yet been forthcoming for this interesting phenomenon, but as shown by Chatterji and Dhar (*Kolloid Zeitsch.*, 1922 XXXI.), peptisation plays an important part in the formation of banded precipitates. In almost all cases where banded precipitates are formed, the phenomenon of peptisation has also been noticed. The facts observed in connection with the formation of these banded precipitates may be summarised as follows:

(1) The phenomenon takes place in a gel in which one of the reacting substances is dispersed.

(2) The spaces above and between the rings are almost entirely free from the reacting substances.

(3) Complex organic matters of a colloidal nature help the taking place of the phenomenon.

If we compare the above facts with those that have been set forth before in the case of pan formation, the similarity becomes at once obvious. The formation of pans in soils is in all probability another example of periodic precipitation on a large scale in nature. At first the soluble salts of iron and aluminium are present in a state of solution throughout the mass of a medium of silicic acid gel. The gel is, of course, formed from the silicic acid sol resulting from the gradual disintegration of rocks by

rain water and their colloidal dispersion. The alkali, naturally present in the soil, or ammonia formed from the organic matter, begins to react with the salts of iron and aluminium producing the insoluble hydroxides, which get precipitated in rings or narrow bands in the silicic acid medium. In course of time the silicic acid gel dries up and gives rise to the typical open texture sandy soil, consisting of quartz grains, the zones of ferric and aluminic hydroxide precipitates forming hard, compact masses, commonly known as "pan."

If this view about the formation of pans in soils is more or less correct, we can easily assign reasons for a number of facts which have been observed in connection with this phenomenon, and which have previously been overlooked. Thus if we scrutinise the analytical figures given above for the pan-bearing soil, it would be found that the iron and aluminium contents of the soil below the pan are much higher than those above, so that there seems as if there is not one layer of pan, but several layers of it close to one another. This is what is expected from the point of view of periodic precipitation. Again, pan-bearing soils are rich in organic matter, and as has been said before, the presence of this considerably enhances the peptising power of the medium and helps in the subsequent formation of banded precipitates. The almost entire absence of calcium carbonate from the soil cannot at present be more satisfactorily accounted for, beyond the fact that the periodic precipitation of substances are specific in nature and that calcium hydroxide or carbonate does not bring about the preliminary peptisation of iron or aluminium hydroxides in silicic acid gel.

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#### FARMING METHODS IN NORTHERN MANCHURIA.

*(Journal of the Royal Society of Arts, July 20, 1923.)*

Northern Manchuria is pre-eminently a country of small landowners. The landowner himself works his fields in the majority of cases, but the larger landowners often turn their farms over to tenants.

The division of the land into small parcels and the low purchasing power of the individual farmer have been serious draw-

backs to the introduction of modern farming machinery, and Chinese conservatism and loyalty to traditions have also been opposed to new methods of farming. In a district covering an area of approximately 250,000 square miles there are, according to information furnished by one of the large dealers in agricultural machinery, only about 300 ploughs of the American type and some 500 German Sack ploughs. There are only 300 disc harrows, and very few mowers, reapers, and self-binders. Even these are not Chinese owned, but belong to Russian farmers who have settled in the zone of the Chinese Eastern Railway.

In Northern Manchuria, according to a report prepared in the American Consulate at Harbin, the land is very carefully worked, great attention being paid to fertilisation. The land is ploughed in parallel ridges and furrows. The soil is worked twice, which enables the roots to draw moisture from the night air, even in time of drought.

The plough used is very primitive. Into a wooden frame is set a spade-shaped ploughshare, which is clamped to the bent wooden lever or beam. The other end of this lever serves as a handle, and at the middle of it is fastened a grader. The ploughshare is held in almost a perpendicular position to the surface of the land and tears it effectively. This plough is usually drawn by two animals (horses, mules, or oxen), and is attended by two labourers, one of whom guides the plough and the other the animals. It is transported to and from the field on a special wooden drag.

There are two methods of ploughing the soil. Either the ploughshare follows the ridge, and where last year there was a ridge there will be a furrow this year, or the ploughshare follows the furrow, and where last year there was a furrow there will also be a furrow this year.

Sowing or seeding is seldom performed by hand, the use of a "chan hu lu" being more popular. This is a dried pumpkin, which has an opening made in the narrow end. The pumpkin is filled with seeds and the opening is then closed with a cork, into which is fitted either a reed or some kind of piping in such manner that the seeds will scatter if the instrument is slightly tipped and lightly tapped with the hand. One workman, carrying the "chan hu lu," walks along the furrow, and tapping the pumpkin with his right hand, he scatters

the seed so that they fall on the ridges. Another man, walking along the ridge, stamps the seeds down with his feet. Behind them follows a third man, with a horse which pulls a small stone roller. This roller follows the two ridges. On the new ridge it levels out the crest, and on the other it smooths out the tracks of the second labourer's feet and covers the seeds with earth.

When weeds begin to appear the Chinese farmer once more follows along the furrows with his plough, deepening them by half a foot so as to surround the sprouts with fresh earth. When the sprouts have reached considerable height the plough is again used for bringing the deeper roots closer to the surface, thus enabling them to absorb more moisture from the air. By this process weeds are also destroyed between the ridges. On the ridges themselves weeding is done by means of hoes.

For the harvest of cereals the Chinese farmer uses a special scythe, which is similar to the American scythe but of smaller dimensions. Very few Chinese farmers in Northern Manchuria are familiar with flails. In threshing, the plants are placed in a circle, with heads toward the centre, and over these is drawn by animals a heavy stone roller. Before the kaoliang is threshed, however, the heads are cut off from the stalks to prevent these being spoiled by the roller, for the kaoliang stalk plays an important rôle on the farm, inasmuch as it is used for roofing, fencing, fuel, and many other purposes. The roller process is continued until all the grains have been removed. Winnowing is done with shovels and old-fashioned hand sifters.

The threshed and cleaned grain is stored either in pits or in specially constructed cylindrical silos, covered with a conical roof. These silos vary in size according to the requirements of the individual farm. They are built of poles, which are plaited with dry twigs, the whole structure being plastered inside and outside with a composition of clay and straw cuttings. It is divided into two or three compartments for the different kinds of cereal. Besides these silos the Chinese employ so-called "chantze." These resemble wells and are made of boards.

The threshed grain is ready for the market and for the feeding of cattle. For preparing human food, however, it is necessary that the hulls be removed. This is done by the "chantze"—a round, sta-

tionary, horizontal millstone, upon which rotates a stone cylinder with a rough surface. This cylinder is usually moved by small donkeys.

The Chinese plough is particularly unsuitable for breaking new ground, and this is one reason why the Chinese farmer is reluctant to take up virgin land. Some years ago the Government conceived the idea of ploughing up large tracts of land in order to sell them to immigrants from the south. It is believed the plan fell through because of some unfortunate financial manipulation in connection with the purchase of machinery. It seems, nevertheless, that this idea may be revived by some enterprising manufacturer, with a view of introducing modern farming machinery on a large scale through the agents of the Government. There appears to be a tendency at the present time to encourage immigration into the Nonni Valley and other parts of Heilungchiang Province.

The Chinese Eastern Railway, which maintains two agricultural experiment stations in the district—one of 300 acres at Station Anda, and one of 250 acres at Old Harbin, together with an experimental farm of 700 acres at Station Echo—appropriated 60,000 gold roubles for farming experiments during the year. The representative of a large American firm has been conducting tractor trials on these grounds, and they are generally reported to be exceptionally satisfactory. Two tractors are being experimented with—one pulling two-bottom ploughs and the other pulling four-bottom ploughs. This representative is of the opinion that the future of these tractors in Northern Manchuria is most encouraging.

The market in Northern Manchuria appears to be worthy of study on the part of manufacturers of agricultural implements, especially the smaller type of implements, such as ploughs, cultivators, seeders, threshers, and fanning mills.

#### THE PREPARATION OF STIBINE FROM ALLOYS.

BY EDWARD J. WEEKS, M.Sc., F.C.S.

Various workers have given the percentage composition of alloys of zinc and antimony best suited for the preparation of stibine, but if these results are summarised

no agreement is found among them. Thus we find the following alloys given:

	Parts of Zinc.	Parts of Antimony.
L. Thompson, <i>Phil. Mag.</i> , 1837, (3), 10, 353 .....	1	1
K. Olszewski, <i>Monatsh. Chem.</i> , 1886, 7, 371 .....	1.5	1
Berthelot & P. Petit, <i>Compt Rendus</i> , 1889, 108, 546 ...	2	1
A. Stock & W. Doht, <i>Ber.</i> , 1901, 34, 2339 .....	4	1
A. Stock & W. Doht, <i>Ber.</i> , 1902, 35, 2270 .....	4	1
	2.5	1

In 1889 Berthelot and P. Petit (*loc. cit.*) stated that no stibine is obtained unless 5 atoms of zinc are present to one atom of antimony. This gives 1 part by weight of antimony to 2.8 parts of zinc.

It is noticed from the above that A. Stock and W. Doht give as the best alloy 2.5 parts of zinc to 1 part of antimony, or 1.35 atoms of zinc to 1 atom of antimony. This does not agree with the statement by Berthelot and P. Petit, and indeed these workers themselves state that stibine may be prepared from an alloy of 2 parts of zinc to 1 of antimony, or 1.09 atoms of zinc to 1 atom of antimony, an experiment which does not agree with their own statement.

We must, therefore, conclude that there is no actual best composition of the zinc, antimony alloy for the preparation of stibine, but that the same amount of stibine may be obtained from any alloy of composition varying from 1 part of zinc to 4 parts of zinc to 1 of antimony.

*Sir John Cass Institute,  
Jewry Street.*

2/8/23.

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### THE INSTITUTE OF METALS.

AUTUMN MEETING, MANCHESTER,  
SEPTEMBER 10 TO 13, 1923.

A very full programme has been arranged, including visits to important works. On the evening of the first day, a lecture will be given by Lieut.-Colonel Sir Henry Fowler, K.B.E., on *The Use of Non-Ferrous Metals in Engineering*, and during the meeting the following communications are expected to be submitted:

E. A. BOLTON, M.Sc., Birmingham, *The Cause of Red Stains on Sheet Brass.*

H. W. BROWNSDON, M.Sc., Ph.D., F.I.C. (Member of Council), *Note on Brinell Hardness Numbers.*

H. I. COE, M.Sc., Swansea, *The Behaviour of Metals under Compressive Stresses.*

HIKOZO ENDO (Sendai, Japan), *On the Measurement of the Change of Volume in Metals during Solidification.*

ULICK R. EVANS, M.A., Cambridge, *The Electrochemical Character of Corrosion.*

MARIE L. V. GAYLER, M.Sc., Teddington, *The Constitution and Age-Hardening of the Quarternary Alloys of Aluminium, Copper, Magnesium, and Magnesium Silicide.*

D. HANSON, D.Sc., C. MARYATT, B.Sc., and GRACE W. FORD, B.Sc., Teddington, *Investigation of the Effects of Impurities on Copper. Part I.—The Effect of Oxygen on Copper.*

DOUGLAS H. INGALL, M.Sc., Wednesbury, *Experiments with some Copper Wire: Cohesion a Function of both Temperature and Cold-work.*

A. H. MUNDEY and C. C. BISSETT, B.A., B.Sc., B.MET., London, *Note on The Effect of Small Quantities of Nickel upon High-Grade Bearing Metal.*

A. H. MUNDEY and JOHN CARTLAND, M.C., M.Sc., London, *Stereotyping.*

HUGH O'NEILL, M.MET., Manchester, *Hardness Tests on Crystals of Aluminium.*

ALBERT M. PORTEVIN, Paris, and PIERRE CHEVENARD, Imphy, *A Dilatometric Study of the Transformations and Thermal Treatment of Light Alloys of Aluminium.*

R. C. READER, Ph.D., M.Sc., Birmingham, *Note on Effects of Rate of Cooling on the Density and Composition of Metals and Alloys.*

E. L. RHEAD, M.Sc.TECH., and J. D. HANNAIL, Manchester, *Crystallisation Effect on Galvanised Iron Sheets.*



PROFESSOR P. SOLDAU, Petrograd, Russia, *Equilibrium in the System Gold-Zinc (based on Investigations of Electrical Conductivity at High Temperatures)*.

Full particulars can be obtained from the Secretary, G. Shaw Scott, M.Sc., 36, Victoria Street, London, S.W.1.

#### THE BRITISH CHEMICAL AND DYE-STUFFS TRADERS' ASSOCIATION.

The Committee of the above Association have forwarded a memorandum from H.M. Treasury, containing proposals that it is suggested may lead to increased shipments of chemicals from this country—as the matter seems to us to be of special importance, we reproduce it in full below:—

[COPY.]

*Memorandum from The British Chemical and Dye-stuffs Traders' Association on the method of payment of duties under The Safeguarding of Industries Act, 1921—Part I.*

Importers of goods scheduled under Part I. of The Safeguarding of Industries Act, 1921, have to pay the duty of 33½ per cent. at the time the goods are landed and cleared at H.M. Customs.

This procedure, it is understood, is governed by Section 39 of the Customs Consolidation Act, 1876, whereby H.M. Treasury are given power to decide whether goods liable to import duties shall be allowed to be bonded or not.

The Treasury Order in respect of The Safeguarding of Industries Act, 1921, stipulated that the duties should be paid at the time of landing and clearance of the goods at H.M. Customs.

During the period this Act has been in force it has been found that the present method of payment of duties as outlined above is, in many ways, having a detrimental effect on the commerce of this country. The following points are submitted in support of this view:

1.—Prior to the introduction of The Safeguarding of Industries Act and the import duties it entails, merchant importers were in the habit of holding as stocks bulk supplies of goods, and were thus enabled to meet both home and overseas demands without delay. The re-exportation aspect

was then of very considerable importance, it being estimated that quite half the volume of imports now liable to Key Industry duty were, when previously allowed free import, disposed of by way of re-export sales. Careful and exhaustive enquiry has been made as to what effect the payment of import duties under the Act has had on this important branch of the chemical trade, and it has been found that:

(a) The difficulties and uncertainty of obtaining "drawbacks" of duties paid at the time of importation make it impracticable for merchants to compete in overseas markets. For instance, unless a merchant holding stocks of goods on which duty under this Act has been paid can ascertain definitely and quickly whether he can recover such duty upon re-exportation, he is unable to arrive at his selling price, and is thus prevented from competing for overseas business. It is certain that if he does not allow for a "drawback" his price to the foreigner would not be competitive.

(b) That on account of this position the volume of re-exports of goods liable to Key Industry duty has fallen away in a very deplorable manner, and merchants are continually complaining that they have, and still are, losing such business, and state that it is largely due to the disadvantages arising out of the present method of collection of duties levied under the Safeguarding of Industries Act, 1921, Part I.

(c) Some firms, in an endeavour to overcome this barrier to re-export trade, are now holding stocks at Continental ports and meeting demands in that way. This must entail loss of freights to the shipping interests of this country; loss of employment at the docks, in warehouses, and in various other directions. It has been found that in this way only is it possible and practicable for merchants in this country to hope to compete successfully in overseas markets.

(d) Claims for drawbacks usually take a considerable time to settle, and in many instances where the goods in question have, since their importation, changed hands one or more times, it has been found almost impossible to satisfy H.M. Customs as to their identity. While the merchant is attempting to overcome these difficulties the overseas business is lost.

2.—As regards sales of dutiable goods in this country, merchants, in order to carry on their business as economically as possible and to fulfil their function as distributors, are in the habit of importing in bulk

quantities. Such goods are gradually liquidated, and in many instances the duty paid at the time of importation may not be recovered in full for twelve months, or even longer. For instance, the importer of dutiable goods to the value of £3,000 has to pay £1,000 as duty at the time of importation, and it is not exceptional for the period mentioned to elapse before the whole of the importation is sold and the duty thus recovered. In this way considerable amounts of capital are locked up, to the detriment of the merchant and trade in general.

It is submitted that, in the case of re-exports, if merchants were given the opportunity of putting goods liable to Key Industry duty into bonded warehouses at the time of importation and thus be relieved of the immediate payment of duty and the uncertainty of obtaining drawbacks, the trade of this country in re-exports of chemicals would be materially facilitated, and would undoubtedly increase in volume.

In the case of sales to buyers in this country, duty would only be paid at the time they were taken out of bond for actual delivery. Under this arrangement comparatively large amounts of capital would be at the importers' disposal, instead of being locked up, as is the case under the present conditions.

Consideration has been given, and enquiry made, as to whether there would be objection on the part of warehouse interests to accepting goods scheduled under Part I. of the Safeguarding of Industries Act, on account of their dangerous character in themselves or when stored with other goods. It appears that as these materials are packed in such a manner as to satisfy shipping lines, who accept them at ordinary rates, and, for the same reason, insurance of such goods is effected at low rates, it is believed that warehouse interests would approve of the suggested system of bonding.

It is therefore suggested that, as the present system of collection of duties under the Safeguarding of Industries Act, 1921, Part I., is doing great harm to the commerce of this country, especially in the matter of re-exports, the Order made by H.M. Treasury at present in force should be suitably amended so as to allow dutiable goods to be put into bond.

*Forwarded to H.M. Treasury, and copy to H.M. Customs.*

*B. C. and D. T. A., London, 4th August, 1923.*

## THE BRITISH CAST IRON RESEARCH ASSOCIATION.

*Monthly Circular.*

JUNE, 1923.

No. 19.

RESEARCH DEPARTMENT.

PROGRESS OF RESEARCH IN HAND.

*Shrinkage Defects Research.*—Experimental castings are continually being made in various foundries. These are being tested under conditions to obtain definite data in respect of chemical and physical properties. Important results bearing upon draws and shrinkages are being obtained.

*Foundry Sand Research.*—Important arrangements are being made for carrying out a thorough investigation upon foundry sands. The work will probably be done at the Birmingham University, and in one of the large foundries. The bureau are issuing a complete bibliography of sand literature.

*Cast Iron to Resist Sea Water.*—A Joint Research with the Electrical Research Association is being arranged to carry out this important work. It is estimated that the experimental work will occupy about two years, and will be carried out at the coast and in tidal rivers. The results of such work will be very beneficial to the electrical industry and our own members.

*Internal Combustion Engine Castings.*—This research, carried out jointly by this Association, the Motor Research Association, and the Motor Cylinder Research Association, is reaching a stage when some beneficial results should accrue. Engine cylinders made in this country and abroad have been examined and reported upon. Test castings to variable specifications have been made, and are now being subjected to test.

*Cast Iron Moulds for Bottle Making.*—This joint research with the Glass Research Association is progressing, and test moulds are now being experimented upon and tried in special bottle making machines.

*Malleable Cast Iron Research.*—It should not be necessary to report every month that the progress of this very important work is hampered by the lack of support given by the malleable industry. Malleable iron-

founders should call a conference and discuss the position of their industry. The Bureau Bulletin gives a complete bibliography of the literature upon malleable iron as published since 1722, which is very interesting reading.

*Standard Specification for Grey Iron Castings.*—The Association considers that the time has arrived when a standard specification for grey iron castings should be drawn up, and steps have been taken to have this carried out in conjunction with the B.E.S.A.

#### PROBLEMS SENT IN BY MEMBERS.

Members, during the past month, have sent in problems for the Director's advice upon the following: Porosity in cylinder castings; defects in pump castings; defective pig iron; annealing malleable iron; liners for semi-Diesel engines; C.I. bevel wheels; Cupola design; pumps for sea water; pin-holes in malleable C.I.; shrinkage in castings; malleable annealing ovens; C.I. valve guards; glass bottle moulds; defects in heavy castings; stripping plate patterns; porosity in malleable castings.

#### THE BUREAU AND LIBRARY.

Further books and papers have been presented to the library during the month. The library, which has been closed for the cataloguing work, is now reopened for issue of books.

The following new foundry book has been sent for review in the next bulletin:

*Pattern Making*, by McCracken and Sampson. Published by Scott Greenwood & Son.

All new books are reviewed in the Bulletin, and members should consult same.

#### MEMBERSHIP.

The gradual increase in the membership is very gratifying. The increase during the past month has been exceptionally good, and places the success of the Association's future work beyond doubt. With trade improving, ironfounders are recognising the necessity of membership, and it only needs the present number to be very materially increased to enable the larger research works to be commenced.

#### SUGGESTIONS FOR RESEARCH.

Members have assisted the Research Committee by making suggestions for re-

search to be carried out. These have been of very great value. The field for foundry research is so great, there are so many problems to attack, that members should advise the Association as to the problems they consider are of the most urgent importance to the industry. Very effective co-operation can thus take place.

Take, for instance, Cupola practice: the Association has assisted a large number of members in their Cupola melting methods, yet it is very remarkable to find the very variable conditions under which this is carried out; there is no standardised practice. Here is a wide field for work by the Association and of vital interest to every grey iron founder in the country, and yet, due either to apathy or to the peculiar foundry conservatism, he holds out in joining the Association and obtaining its advice.

#### INTERNAL COMBUSTION ENGINE CYLINDER RESEARCH.

"The continued examples of failure of metal, not necessarily confined to the marine Diesel engine industry, seem to indicate that metallurgical science either has not reached the high standard which we have lately been accustomed to believe, or the results of investigation in working practice and in experimental research are not communicated in a sufficiently extensive manner to those concerns immediately or indirectly interested. In the case of Diesel engine construction it appears particularly advisable that no efforts should be spared in the direction of further research, and, what is of vital importance, the publications of specifications of alloys, records of experiments with relation to the behaviour of metals in high temperatures, and data referring to wear of parts.

"We believe that much time and labour could be saved if there were more co-operation between marine Diesel engine builders, particularly with regard to their experimental sections. Undoubtedly, with such involved subjects demanding investigation, collaboration would benefit the largest concerns equally with the smallest. Definite standards could be set up, guess-work and rule of thumb practices abolished, and data of exceptional value afforded. With reference to specifications of metal, doubt as to the capabilities of certain types of cast-iron has led to a plethora of costly expedients, by which the designer, bringing to his aid constructional complications, aims at a result which should be attained by more

direct and simple means. The present work of the British Cast Iron Research Association should be valuable in this direction."—(*Motor Ship*, June, 1923.)

Central House, New St., Birmingham.

THOS. VICKERS, *Secretary*.

### ROYAL INSTITUTION OF GREAT BRITAIN.

WEEKLY EVENING MEETING, FRIDAY, MAY  
4, 1923.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D.,  
F.R.S., TREASURER AND VICE-PRESIDENT,  
IN THE CHAIR.

### THE ORIGINS OF THE CONCEPTION OF ISOTOPES.

A Lecture delivered by Frederick Soddy  
M.A., F.R.S.

One of the most important consequences of the study of the chemistry of the products of radioactive change has been the discovery of isotopes and the interpretation in consequence of the Periodic Law in terms of modern views of atomic structure. It is one of the few fields in the vast borderland between physics and chemistry, overrun of recent years by an advancing swarm of mathematicians and physicists, armed with all sorts of new-fangled weapons, in which the invaders have found the chemist already in possession. The broad highways they have hewn thereto are already dusty with the tread of pilgrims, and are being watered by the tears of candidates for "Honours." But the somewhat intricate bye-ways through which the chemist first found his way into this virgin territory, and the views on the road before it was in sight, may still preserve something of their pristine interest.

The word *isotope* signifies "the same place," in allusion to isotopes occupying the same place in the Periodic Table. Before this word of theoretical meaning was coined, isotopes were experimentally well known as elements non-separable by chemical methods and completely identical in their whole chemical character. The analysis of the constituents of matter, to which we were born and brought up to regard as the most searching and fundamental, is an

analysis by means of its chemical properties. Although, later, a new and even more powerful method, spectroscopic analysis, was developed, it merely dotted the *i*'s and crossed the *t*'s of chemical analysis, filled in a few vacant places in the Periodic Law, and handed over the newcomers to the chemist to classify along with the rest of the eighty or so "foundation stones" of which he supposed the material universe to be built up. Then, with the close of last century, another new method, radioactive analysis, was developed, which is applicable of course only to the radio-elements—that is, to the elements uranium and thorium and the thirty-four, as we now know, successive unstable products of their spontaneous disintegration. Each of these possesses a definite radioactive character; it is produced from one and changes into another element, and, in both changes, rays characteristic of the two substances are expelled, which are as fine a hall-mark of their identity as any of the "tests" of chemical analysis. But radioactive character, unlike spectroscopic character, is completely independent of chemical character. The latter might be called "existence properties," whereas the radioactive character is that attending the explosion of the atom which terminates the existence of the element as such. It provided the necessary independent method of analysis capable for the first time of distinguishing between elements identical chemically and occupying the same place in the Periodic Table—*i.e.*, between isotopes.

### THE EARLIER CHAPTER OF RADIO-CHEMISTRY.

Not a hint of this, however, was afforded by the earlier chapter of radio-chemistry. On the contrary, no development could appear more normal. Just as rubidium, thallium, etc., were detected by the spectroscope before anything of their chemistry was known, so radium was detected in pitchblende by its radioactivity in concentration thousands of times less than is necessary to show a single line of its spectrum. But with more concentrated preparations a new spectrum *was* discovered, and then a new element, which was found to possess a chemical character entirely new and sufficing for its separation in the pure state from all other elements. As in the case of the elements discovered by the spectroscope, radium was found to occupy a place, hitherto vacant, in the Periodic Table. But as it happened radium is exceptional in this. Its chemical character

was quite normal, and indeed could have been largely predicted beforehand for the missing element occupying this place. The development of the subject showed it to be but one of some thirty-four radio-elements formed from uranium and thorium. But there are not thirty-four vacant places in the Periodic Table to accommodate them.

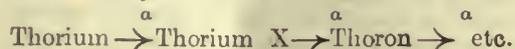
#### META-ELEMENTS.

So far as I am aware, there is no anticipation, prior to the systematic study of the chemistry of the radio-elements, of the idea that there may exist different elements with absolutely identical chemical character. Sir William Crookes, it is true, once thought, though the idea has not survived more extended examination, that the properties of the elements, as we know them, might be a mean value, and that the individual atoms composing the element might differ in weight and chemical character continuously on either side of this mean. If so, more refined methods might serve to resolve the element into a collection of what he termed "Meta-Elements," possessing the main character of the original, but differing from one another to a slight extent. Misled by the phosphorescence spectra, which are now known to be characteristic of mixtures rather than chemically homogeneous substances, he thought at one time that he had been successful in resolving yttrium. But the present idea that elements may exist, absolutely the same in chemical nature and yet absolutely different in other properties, such as radioactivity and atomic weight, is totally distinct from this.

#### THE EXPERIMENTAL METHOD THAT FIRST REVEALED ISOTOPES.

I venture to think that no more elegant extension of our methods of gaining new knowledge has ever been obtained than that which, in due course, was to reveal the existence of isotopes. The original observations, upon which the theory of atomic disintegration was first founded, were that thorium is continuously producing a new radioactive substance, thorium X, separable from it by precipitation with ammonia, but not with other precipitants, and, after separation, continuously re-forming again. The thorium X was short-lived, and changed again into a gas, the thorium emanation, for which the name thereon has recently been proposed, which was even shorter-lived and changed again to a solid, the "excited activ-

ity," now known as the active deposit, which again went through further changes. The rays resulted from these successive changes,  $\alpha$ -rays in the first, and  $\alpha$ -,  $\beta$ - and  $\gamma$ -rays in the last changes. Below is the first part of the thorium disintegration series as it appeared to Sir Ernest Rutherford and myself in 1903:—



In 1905, Sir William Ramsay and O. Hahn were engaged in extracting radium from thorianite, a new Ceylon mineral containing both uranium and thorium in important quantities. The radium was separated with the barium, and the chlorides fractionated in the usual way. They found a new radio-element to be present, and to be separated from the radium with the barium. It proved to be the direct parent of thorium X, and intermediate in the series between the latter and thorium, and they called it radiothorium. In spite of this easy and apparently straightforward separation, the experience of a number of chemists showed that something remained to be explained, for it was found to be difficult to the verge of impossibility to separate radiothorium from thorium. Ramsay and Hahn had in fact "separated" isotopes in 1905, for radiothorium and thorium are isotopes. Yet further work has shown the two to be so alike that no separation by chemical means is possible!

Then in 1907, along with the radium which had been separated from thorianite, Hahn discovered another new radio-element, mesothorium, the direct parent of radiothorium and intermediate between it and thorium. In the next year he showed that mesothorium consists of two successive products—the first, the direct product of thorium, mesothorium 1, being practically rayless and generating a short-lived product, mesothorium 2, giving powerful  $\beta$ - and  $\gamma$ -rays.

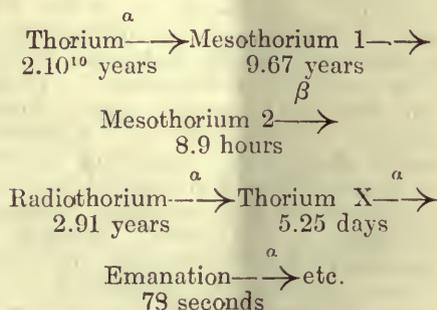
This resolved the mystery, and one cannot do better than to quote the words of McCoy and Ross (*J. Amer. Chem. Soc.*, 1907, XXIX, 1709):

"Our experiments strongly indicate that radiothorium is entirely inseparable from thorium by chemical processes. . . . The isolation of radiothorium from thorianite and from pure thorium nitrate . . . may have been accomplished by the separation of mesothorium, which in time changed spontaneously into radiothorium."

Thus the radiothorium separated from

the mineral thorianite by Ramsay and Hahn was not the radiothorium in the mineral, but that subsequently produced from the easily separated mesothorium, after it had been removed from the thorium. If they had fractionated the radium-mesothorium-barium mixture at once they would not have discovered radiothorium. The lapse of time after the separation of the mesothorium is essential. Nowadays many non-separable radio-elements are, like radiothorium, "grown" from their separable parents. Thus radium D, an isotope of lead, is grown from the radium emanation (radon), although it cannot be separated from the mineral, which always contains lead in quantity.

The first part of the thorium series now runs\* :—



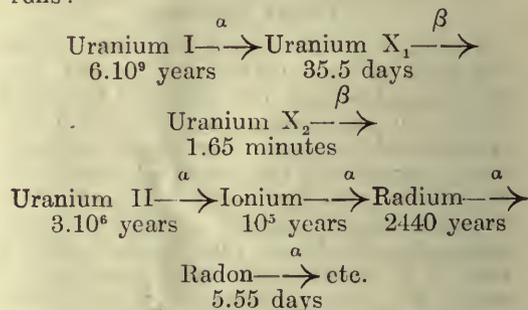
In this series thorium and radiothorium and mesothorium and thorium X are two pairs of isotopes. If we represent the successive products by balls of different colours to indicate their chemical character, isotopes being of the same colour, chemical analysis will sort the balls into their different colours, and the lapse of time will cause some of the colours to change. The ball representing mesothorium will in time turn into that representing radiothorium, so that the latter, before indistinguishable from thorium, becomes known as a separate individual.

#### THE ISOTOPES OF URANIUM.

It will be noted that the method of separating isotopes depends upon their being alternate rather than successive in the series. If radiothorium had been the direct product of thorium, the two would

never have been separated to this day. The changes of chemical character are, as we shall later see, intimately connected with the electric charges on the  $\alpha$ - and  $\beta$ -particles expelled. For successive products to have the same character no rays, or at least no charged particles, must be expelled. It is always as well—and no subject illustrates the point better than that of isotopes—to reflect not only upon what our methods are able to reveal, but also upon what they cannot reveal.

At first it seemed as if uranium itself was a case of successive isotopes. Boltwood, in 1908, proved from his study of the relative activities of the successive products giving  $\alpha$ -rays in minerals, that whereas all of them, except uranium, gave off only one  $\alpha$ -particle per atom disintegrating, uranium gave off two. By direct observation with the scintillation method it was proved that the two  $\alpha$ -particles from uranium are *not* simultaneously expelled, and later it was shown that they possess different velocities. If the slower comes from uranium itself (uranium I), the period of which is known to be  $6.10^9$  years, the swifter must come from the isotope (uranium II), and its period must be some three million years. This is an example of isotopes being revealed by difference of radioactive nature simply, though no other evidence of their separate existences is available. Owing to the long periods of the  $\alpha$ -ray giving members of the early part of the uranium series, it has been much more difficult to unravel than the thorium series. As a result of researches too numerous to detail, it has been concluded that the main series is almost entirely analogous to the thorium series, and runs:—



Though two short-lived products probably intervene between the two uraniums, analogous to the two mesothoriums between thorium and radiothorium, the relation of their period to that of their product, uranium II, is so hopelessly unfavourable that

\* The periods shown in the second line are the periods of average life of the successive products. These are 1.443 times the period required for one-half of the element to change.

there is no hope of ever being able to put the separate existence of uranium II into evidence in the same way as was done for radiorium. For all *practical* purposes the two uranums are as non-separable by this method as if they were actually successive products. I spent many years, before this part of the series was at all well known, looking for the product of uranium X, and separated this constituent from 50 kilograms of uranium nitrate repeatedly in the attempt. I was looking for a growth of  $\alpha$ -rays concomitantly with the decay of the  $\beta$ -rays of the uranium X. If the product had been ionium, as at first thought

(U I—<sup>a</sup> U II—<sup>a</sup> U X— <sup>$\beta$</sup>  Io—<sup>a</sup>), it should have been just possible to detect it. But since it is the thirty times longer-lived uranium II, the attempt is hopeless, especially as uranium X and ionium are isotopes, and therefore the uranium X separated must always possess a certain initial  $\alpha$ -activity due to ionium.

#### THE ABSOLUTE CHEMICAL IDENTITY OF ISOTOPES AND ITS IMPLICATIONS.

The years 1908-1910 were productive of many prolonged and serious efforts to separate isotopes by chemical means. In 1908 Boltwood discovered ionium, and showed that it resembled thorium. Keetman, who with Marckwald discovered ionium independently, tried twelve good methods, all known to be effective, in the purification of thorium in the attempt to separate the ionium from thorium, completely without success. Auer von Welsbach, on a technical scale, separated the ionium and thorium from 30 tons of pitchblende, and tried fresh methods in the hope of separating them, but failed. It was with this preparation that Exner and Haschek tried without success to find the ionium spectrum, and Russell and Rossi confirmed their result, that the spectrum was that of pure thorium. When later I had determined beyond doubt, from measurements of the rate of growth of radium from uranium, that the period of ionium was 100,000 years, and that Welsbach's preparation must have been approximately 30 per cent. ionium and 70 per cent. thorium by weight, it followed that the spectra of isotopes must, like their chemical character, also be identical. The difference, if any exists, is almost beyond the limit of detection by the most powerful methods.

(To be Continued.)

#### £15,000 DONATION TO IMPERIAL COLLEGE OF SCIENCE.

It is with pleasure that we are able to record an offer by the Clothworkers Company of the City of London of an annual contribution of £3,000 for the period of five years, 1923-1927, to the Governing Body of the Imperial College of Science and Technology, South Kensington, to be applied towards the maintenance and development of the City and Guilds (Engineering) College, one of the three constituents of the Imperial College of Science. This donation is supplemental to the sum voted some years ago by the Goldsmiths' Company, a gift amounting to £85,000, which enabled the Engineering College to extend its premises, and is quite distinct from the annual vote of £5,000 from the City and Guilds of London Institute, which has been paid to the Imperial College since the Charter was granted some fifteen years ago and applied to the City and Guilds (Engineering) College. It is another indication of the value which practical men in the City of London attach to the research and general teaching in science, specially in relation to industry.

#### BOOKS RECEIVED.

*Landolt Börnstein, Physikalisch-Chemische Tabellen*, by DR. WALTHER A. ROTM and DR. KARL SCHEEL. 2 Vols. Pp. XV. + 1695. 1st Ed., 1923. Verlag von Julius Springer, Linkstrasse 23-24, Berlin, W.9.

*The Discovery of the Nature of the Air and of its Changes during Breathing*, by CLARA M. TAYLOR, M.A. Pp. IX. + 84. 1st Edition, 1923. Messrs. G. Bell & Sons, Ltd., York House, Portugal St., London, W.C.2. 1s. 6d. net.

*Materie Elektrizität Energie*, by DR. WALTHER GERLACH. Pp. 195. 1923. Verlag von Theodor Steinkopff, Dresden und Leipzig.

#### BULLETINS PUBLISHED BY THE U.S. DEPARTMENT OF THE INTERIOR.

*Cadmium in 1922*, by C. E. SIEBENTHAL and A. STOLL.

*Petroleum in 1919-1921*, by G. B. RICHARDSON.

*Natural Gas in 1919-1921*, by R. S. McBRIDE and E. G. SIEVERS.

732: *Geology and Ore Deposits of Shoshone County, Idaho*, by JOSEPH B. UMPLEBY and E. L. JONES, JUN. Pp. V. + 156.

740: *Mica Deposits of the United States*, by DOUGLAS B. STERRETT. Pp. XI. + 342.

741: *The Jarbidge Mining District, Nevada, with a Note on the Charleston District*, by FRANK G. SCHRADER. Pp. V. + 86.

743: *Geology of the Oatman Gold District, Arizona; a Preliminary Report*, by F. L. RANSOME. Pp. IV. + 58.

#### WATER-SUPPLY PAPERS.

488: *The Floods in Central Texas in September, 1921*, by C. E. ELLSWORTH. Pp. IV. + 56.

493: *Hydroelectric Power Systems of California, and their extensions into Oregon and Nevada*, by FREDERICK HALL FOWLER. Pp. XLIX. + 1276.

#### NOTICES OF BOOKS.

*La Tannerie au Maroc*, par CH. ZEIGLER. Pp. 122. Paris: Edité par "La Chaussure Française," Boulevard Sebastopol. 1923. Price 7fr. 50.

The native leather trade in Morocco has always been prosperous, cattle rearing being a simple matter, and various vegetable bodies suitable for tanning are to be found near to hand. The processes are still conducted in a primitive manner, almost identical with those employed in England during the seventeenth and the beginning of the eighteenth centuries. The French have, however, recently introduced certain improvements.

Three kinds of tanning bodies are used, viz., crudely crushed oak bark, Tizra (*Rhus pentaphylla*), and Takaout (the gall of *Tamarix Articulata*).

The Tizra is a tree which seldom attains more than eight feet, but the bark of the trunk contains about 13 per cent. of tannins. The bark of the roots and branches is also used.

Several varieties of tamarix gall are known, and usually contain 40 per cent. of tanning matter. It is used especially for sheep and goat-skins.

The bark of three species of oak, *Quercus suber*, 2. *ilex*, and 2. *coccifera*, are also employed. Certain other native plants are quoted as having slight application.

For making leather, the skins are first depilated by immersion in several baths of milk of lime of increasing strength. They are then thoroughly washed and scraped, and it is customary to steep the skins for a week in water, to which dried figs have been added. The sugar present in this bath is supposed to give a suppleness to the leather. The actual tanning is then conducted in a bath of one or other of the bodies mentioned, and lasts about three or four days.

The processes throughout are most unhygienic, and are usually carelessly conducted. Further, although the leather so produced can be of a high quality, its value is often diminished by faults in the skin, due to careless killing of the beasts, and sometimes to the presence of parasites.

The author has described the preparation of the skins and their sale in the markets, and gives other details of general interest, together with numerous photographs and some coloured illustrations of native shoes.

J.G.F.D.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 18573—Ostro-Products Corporation of America.—Manufacture of medical preparations containing arsenic. July 16.  
 18574—Ostro-Products Corporation of America.—Manufacture of paraoxymetanitrophenyl-arsenious acid. July 18.  
 18362—Carbide & Carbon Chemicals Corporation.—Purifying chlorine, &c. July 16.  
 18439—Naugatuck Chemical Co.—Process for halogenating latex, &c. July 17.  
 18552—Shimadzu, G.—Manufacture of powder of lead suboxide intermingled with powder of metallic lead. July 18.

#### Abstract Published this Week.

- 198576—Metaldehyde. J. Y. Johnson, 47, Lincoln's Inn Fields, London.

*Metaldehyde* is produced by the action of the following catalysts on acetaldehyde at temperatures below 10° C., (1) titanium chloride, (2) a bromide of an alkali or alkaline-earth metal, such as lithium or calcium bromide, (3) a halide of an alkali metal, alkaline-earth metal, aluminium, zirconium, thorium, cerium, lanthanum, yttrium, ytterbium or titanium, in conjunction with an acid, such as hydrochloric or hydrobromic acid, an acid salt, or a compound having acid properties, such as ferric chloride, aluminium chloride, or sulphur and antimony haloids.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.



## THE CHEMICAL NEWS,

VOL. CXXVII. No. 3305.

## SIR WILLIAM CROOKES' ANTI-GLARE GLASSES.

By J. H. GARDINER, F.INST.P.

I suppose that I have the privilege of knowing as much as anyone about this subject, having been intimately associated with the late Sir William Crookes for more years than I care to count, working under him in all the researches connected with the glasses that bear his name. Sir William was deeply interested in the subject, and was engaged upon the work at the time of his death.

A few words briefly giving the history of the research may not be out of place. The work on the radiation transmission of transparent substances began with an enquiry into the cause of glass-maker's cataract, and several years of hard work were devoted to it; in 1914 a paper was read before the Royal Society in which formulæ were given for many glasses having special optical properties, and manufacturers were encouraged to produce them for general use. As a result, Sir William was inundated with enquiries from private people needing assistance for eyesight trouble, and from glass manufacturers who wished to use his name for glasses that they had succeeded in making from his published formulæ.

It soon became evident that further work was necessary to produce a glass that would absorb as much ultra-violet radiation as possible, and at the same time transmit the bulk of the visible rays; the glass also had to be pleasing in appearance. It was evident that it would be necessary to make a variety of tints to suit different climatic conditions.

The work was carried out with the assistance of Mr. Harry Powell, of Whitefriars Glass Works, whose death unhappily occurred a few days ago. Agreements were made between Sir William and Mr. Nelson Wingate, of Wigmore Street, W., for the glasses to be placed upon the market as soon as conditions made their production possible. Some of these glasses are on exhibition here to-night. Many causes, that I need not enter upon now, have prevented very large production, but it is hoped that the output will be increased shortly; the

glass is of a very special character, and presents unexpected technical difficulties.

On the death of Sir William the whole of the data for the preparation of the glasses, and the apparatus that had been devised for obtaining measurements of the radiation transmitted and absorbed by them, were given into my charge; the apparatus will shortly be erected at the Laboratories of the new Whitefriars Glass Works at Wealdstone, where we hope to be able to produce the material in larger quantities than has been possible at the old works in London.

## DISCUSSION.

Dr. L. C. Martin: I would like to draw attention to the work of Verhoeff and Bell on the "Pathological Effects of Radiant Energy on the Eye" (*Proc. Amer. Acad. Arts and Sciences*, July, 1916, LI., No. 13). A systematic review of the literature is given by Dr. C. B. Walker in the same issue. The authors show that the radiations possessing "abiotic" power (or power of destructive action on living tissue) are confined to wave lengths shorter than  $0.305 \mu$ . It is under exceptional conditions that such harmful action can be caused by sunlight which possesses very little energy at  $0.305 \mu$  and contains no wave lengths shorter than  $0.295 \mu$  at the earth's surface owing to atmospheric absorption. Similarly the possibility of abiotic action with the light from ordinary enclosed sources of artificial light is very remote; although with naked arcs, etc., special protection must be given.

In ordinary life the causes of eye strain and inflammatory conditions must be sought in conditions other than the abiotic action of light, and attention would be better directed to the regulation of the intensity of the visually apparent radiations, to general health, and to the provision of proper refractive correction. The conclusions set out in my paper on "Light Filters for Eye Protection" (*Trans. Opt. Soc.*, April, 1917, XVIII.) agree with those of Verhoeff and Bell, and I would like again to draw attention to that paper in the present connection.

Mr. H. H. Emsley: I associate myself with Dr. Martin to the extent of expressing some confusion of mind as to what exactly Crookes' glass is intended to do. My recollection of Crookes' work on the subject is that it was found that cataract in glass-workers' eyes was caused by the infra-red radiation and not by the ultra-violet. Nowadays one hears no word about the infra-red absorbing properties of the glass. It is true

that Crookes extended his investigation as he proceeded and encountered many difficulties, but I am not clear as to why the ultra-violet is continually referred to and practically nothing is stated about the infra-red.

(From "Transactions of the Optical Society," Vol. XXIV., No. 2, 1922-1923.)

### SOME PROPERTIES OF THE METAPHOSPHATES OF SILVER.

By JOHN MISSENDEN, B.Sc., AND F. E. LIECHTIL.

The *di*-salt, which is mainly produced by the action of the nitrate upon an alkaline metaphosphate, is of a curiously hard crystalline structure, insoluble in water; nor is any water released from the substance by heating to dull redness. It is quite possible, however, to prepare a monohydrated *di*-salt (*i.e.*, the *monohydrated silver dimetaphosphate*,  $\text{Ag}_2\text{P}_2\text{O}_6\text{H}_2\text{O}$ ) in the following reaction: Add to a solution of silver nitrate about one-half by weight of lithium disodium metaphosphate, and gently apply heat until evaporation has dispelled 30 per cent. of the water. The crystals will separate upon cooling.

In a similar way, the *monohydrated silver trimetaphosphate*,  $\text{Ag}_3\text{P}_3\text{O}_9\text{H}_2\text{O}$ , may be obtained from the action of the nitrate upon a concentrated solution of sodium trimetaphosphate. Some doubt was expressed as to the correct proportions of the constituents. A. Weisler, used three times as much of the nitrate as the trimetaphosphate, but C. G. Lindböm<sup>2</sup> was successful with an excess of the latter. The writers have found, however, that equal proportions give the best results; but a most interesting point is that far larger crystals can be obtained if the metaphosphate is in excess, although sodium comprises part of their content up to (and, in rare cases, over) 0.45 per cent. The monohydrated silver trimetaphosphate has been found to yield 64.2 per cent. of its water at 100° C., but reabsorbs the greater part from the atmosphere, and will not make a further yield when reheated to a similar temperature, although the whole of the water is lost upon liquefaction.

The *hexametaphosphate*, obtained in gelatinous white flakes, takes the formula,  $\text{Ag}_6\text{P}_6\text{O}_{18}$ , and is quite insoluble in water. It can be prepared, however, in a decided crystalline form, and may be divided into silver tetraphosphate,  $\text{Ag}_4\text{P}_4\text{O}_{13}$ , and an acid solution. Treatment with sodium sulphide produces sodium hexametaphosphate.

By the action of silver nitrate upon the slightly soluble sodium dimetaphosphate, a new compound, *silver decametaphosphate*,  $\text{Ag}_{10}\text{P}_{10}\text{O}_{30}\text{H}_2\text{O}$ , is formed, which lost the greater portion of its water upon heating to 135° C. The most stable form of this compound is the tetrahydrated salt. The action of silver nitrate upon sodium hexametaphosphate gives two more compounds, *sodium pentasilver hexametaphosphate*,  $\text{Na Ag}_5(\text{PO}_3)_6$ , and *disodium tetrasilver hexametaphosphate*,  $\text{Na}_2\text{Ag}_4(\text{PO}_3)_6$ . By using a potassium hexametaphosphate,  $\text{K}_2\text{Ag}_4(\text{PO}_3)_6$  has been produced, but we do not believe that the potassium pentasilver salt exists.

W. Henneberg's theory that the interior of the grey viscid mass produced by the action of hot water upon silver hexametaphosphate is composed of *silver pyrometaphosphate*,  $\text{Ag}_4\text{P}_2\text{O}_7\text{Ag}_2\text{P}_3\text{O}_6$ , is well founded, but the mass only contains about 40 per cent. of this compound, the remainder being silver tetraphosphate,  $\text{Ag}_4\text{P}_4\text{O}_{13}$ .

A. V. Kroll<sup>3</sup> has discussed a series of the order  $\text{Ag}_2\text{O} : \text{P}_2\text{O}_5 :: 1 : 2$  (and as 1 : 3). He has termed them the ultraphosphates. Little is known of this series.

### FISH MEAL AND GUANO.

J. O'SULLIVAN.

Endeavours hitherto made for the manufacture of fish meal and guano have, in some cases only, when favoured by circumstances, given good results. The chief causes why manufacture has not been more widely adopted are: unsuccessful local attempts; high cost of plant; the low prices of the products and, especially, doubts as to which were the best methods. The question now presents itself in quite a different light. In the first place, the laws regarding destruction of refuse are very strict, and it is more expensive for those re-

<sup>1</sup> *Zeit. anorg. Chem.*, 1901, XXVIII., 177.

<sup>2</sup> *Acta Lund.*, 1844, X., 7.

<sup>3</sup> *Ueber Ultraphosphate. Zeit. anorg. Chem.*, 1912, LXXVI., 408.

sponsible, and then the products, at the present time, realise relatively good prices. Moreover, it has been made possible to transform fish oil into solid fat by hydrogenation and sell it for various industrial purposes. The protein, after suitable treatment, can be utilised as food for animals (especially pigs), so that prices are quite likely to be higher than those for the guano. Finally, a number of engineering firms have undertaken a scientific study of this question, hitherto neglected.

From the technical point of view, the problem can be epitomised in one condition, viz., complete separation of the three component parts, water, fat, and dry matter. The simplest mechanical methods consist in treatment of the raw materials in a hydraulic press or under heated rollers. Results have not been satisfactory. In the first case the water and fat are not completely extracted, and the meal has to be subsequently desiccated. The following is an analysis of meal made with hot rollers which have the same inconvenience as presses:—

Whole Meal.—Crude protein, 58.29 per cent.; fat, 23.79 per cent.

Herring Meal.—Water, 8.32 per cent.; crude protein, 58.91 per cent.; fat, 14.02 per cent.

The percentage of fat is much too great, and this can only be employed as a fertiliser and not as food, which would give flesh and milk an oily flavour. The chemical methods are very numerous. Treatment with sulphuric acid, sulphuric saponification, is often adopted, and gives better separation of the fat than by boiling the materials in presence of sulphuric acid. After pouring off the fat the solid residue is neutralised, dried and crushed or treated with nitro-sulphate of calcium. Another method is boiling the fish waste under pressure, mixed with caustic soda. The cells are broken up and the fat saponified. The soap is obtained by precipitation, and the residue dried and crushed.

Finally, the materials are transformed into a fertiliser by aid of a potassium salt, to be then dried. The chemical processes have been but little studied from the constructive point of view, and the plant is generally very rudimentary. The chief defect is that the products are only fit for fertilisers and results of manufacture consequently less favourable. The process by displacement (solvents like benzine, carbon tetrachloride; and all derivatives of chlorine, methane and ethane) removes fat

sufficiently, and gives a residue in form of a fertiliser, after drying and crushing. Consequently this method has acquired greater importance and been more carefully studied. Analysis of a meal made from haddock with benzine gave: water, 14.3 per cent.; protein, 58.55 per cent.; crude fat, 1.76 per cent.; dry residue, 15.67 per cent. Solvents, however, cause certain difficulties. The crude material is made impermeable by benzine, and must be treated on a surface. Then, as the percentage of water in the fish is great, the consumption of solvents is also great. The thermochemical method gives the best results, the materials being treated with steam under pressure which separates the fat and the dry residue can then easily be treated. The toxins in the fish are destroyed by the steam, and the meal obtained can be used as a feeding stuff for animals. After having made a study of this new problem, a firm of Zurich (Messrs. Escher, Wyss & Co.) have solved it by aid of a very simple and inexpensive plant which gives all the advantages of the thermochemical method for treating large quantities of fish, 4 to 6 metric tons, in 10 to 12 hours. This installation comprises: (1) A horizontal autoclave (extractor) with a double heating jacket and perforated rotary drum inside. The mouth of the autoclave is at one end. The drum is worked by pulleys and an endless screw; (2) a vertical vessel, to which the autoclave is connected, communicating by pipes with (3) a continuous press above the autoclave and resting on a gallery; (4) a fat pan fed by the press; (5) an air pump for the autoclave; (6) a steam boiler; (7) an electric motor driving the autoclave drum, pump and press. Working is as follows:—

The fish waste is put into the perforated drum, the autoclave being then shut hermetically. Hot steam is then admitted, the drum rotating continually. A mixture of oil, solid and liquid substances, run through the openings in the drum into the vertical vessel, where they separate by gravitation. When everything in the autoclave has been run off, the fat which collects on the top is drawn off, leaving the liquid and solid matter in the vessel to pass through the pipes into the press, which separates much of the water and fat from the solids.

The oily liquid runs into the pan fed by the press, and the solid parts fall through an opening into the autoclave. Then the latter is shut, and again heated, the drum, which is furnished with agitators on the

circumference, being set in motion. The air pump produces a vacuum in the autoclave, which makes desiccation easy. This pump is also used to draw off the fumes which are then got rid of by condensation. The crude, dry materials are automatically discharged from the extractor, simply by making the drum rotate in the opposite direction. A little boiler supplies steam, and a 9 h.p. electric motor power. Thus this plant is very simple and highly efficient. Consumption of steam is reduced to a minimum in drying the meal, as much of the water in the fish is previously extracted and that of coal is also very small, scarcely 15 per cent. of the weight of the fish.

The meal produced is thus much freer from fat than in the ordinary thermochemical method, as the following analysis demonstrates: water, 12 to 15 per cent.; fat, 6 to 8 per cent.; residues, 13 to 28 per

Groups of pigs.	Boiled potatoes.	Waste flesh.	Potato Flakes.
a	4	0.5	0.172
b	4	0.5	0.172
c	4	0.5	0.172
d	4	0.5	0.127

Calculations made after killing the pigs demonstrate that the amount of meal (in kilogrs.) to obtain a nett increase, in weight of the pigs, of 100 kilogrammes, is:—

Groups.	Weight.	Assimilable Protein	Weight of meal equivalent to the assimilable protein.
a	399	54.12	123
b	386	52.32	118
c	388	52.46	114
d	366	49.54	108

cent. These residues themselves contain phosphate, 5 to 7 per cent.; crude protein, 46 to 52 per cent.; non-nitrogenous matter, 6 to 14 per cent. The great value of the method, however, is due to the fact that the meal can be used as a feeding stuff, and results have been so encouraging that it is not rash to assert that this method will grow more and more important, all technical difficulties having been overcome and good plant available. The feeding value of fish meal has been illustrated experimentally with the following results:—

Dry			
Meal.	Matter.	Protein.	Fat. Residues.
I.	87 p.c.	48.9	2.1 25.6
II.	81 p.c.	51.5	4.8 13.5

Two groups of pigs were fed with one quality of meal, the daily rations being as follows in kilogrammes:—

Maize.	Meal.	
	I.	II.
0.263	0.568	
0.263	0.568	
0.263	—	0.548
0.263	—	0.548

The flesh of the pigs was of the finest quality and without any odour of fish. The commercial yield will, of course, depend upon quantity and quality of the raw materials. However, the following may be taken as example: 2 to 10 per cent. fat and 15 to 35 per cent. meal. The profits realised by treating 4 to 6 metric tons of fish per day, to obtain 3 per cent. fat and 20 per cent. meal, were 56,400 francs for the year, which is regarded as very satisfactory. The method described reduces the bad odours to a strict minimum, and they cause no inconveniences. — (*Revue Général du Froid, June-July, 1922.*)

### DESCLOIZITE FROM SOUTH-WEST AFRICA.

BY PERCY A. WAGNER, ING.D., B.Sc.,  
F.G.S., M.A.I.M.M.E.

(Communicated by permission of the Honourable the Minister for Mines and Industries.)

Superficial deposits of vanadium ore are worked at a number of localities in the Grootfontein district of the South-West Protectorate and form the basis of quite an im-

portant industry. The ores occur for the most part in sand or rubble-filled solution cavities and *karrenfelder* in the surface of the Otavi dolomite, most rarely in open solution fissures and in surface breccias, and finally as actual replacements of the dolomite, these being, however, always connected with one or another of the previously mentioned types of deposit.

Some of the occurrences have descloizite as the predominant ore mineral, others mottramite, and yet others (Berg Aukas) ap-

parently vanadinite.<sup>1</sup> Excellent descriptions of some of the earlier discovered occurrences have been published by H. Schneiderhöhn,<sup>2</sup> but no comprehensive study of the deposits has as yet been made. It is evident, however, from what is known, that these are all of the nature of residual accumulations formed by the concentration, at favourable *loci*, by descending meteoric waters of small amounts of vanadium disseminated through originally overlying deposits of copper-lead-zinc ore in the Otavi dolomite or the ore-bearing aplite intrusive in that formation.<sup>3</sup> As the vanadium compounds are the last to survive the degradational processes, they are evidently peculiarly resistant to chemical erosion, which is all powerful in a karst region such as that under review.

The object of the present note is to describe some exceptionally handsome specimens of descloizite ore recently sent to the writer by Mr. C. G. C. Clarke, of the South-West Africa Company, Limited. They are from two localities, namely, the farm Olifantsfontein West, situated 12 miles north-west of Grootfontein North, and the farm Abenab, situated 20 miles north of Grootfontein.

At the former, according to the description accompanying the specimens, the deposit takes the form of a well-defined vertical cleft in the dolomite, the walls of which are lined with dark lustrous crystals and crystal aggregates of descloizite forming continuous crusts, several superimposed crusts being in places present.

In the material sent to the writer, the crystals range in length from a millimetre and less to 1.7 cm. Actually the largest had a length, measured along the *c* axis, of 1.72 cm., and a breadth measured along the *b* axis of 0.8 cm. They are made up of the unit pyramid and the unit prism, the faces of the latter being generally horizontally furrowed owing to an oscillatory combination of the two forms. More rarely the pyramidal faces are terraced owing to the same cause. The habit of the crystals is sometimes prismatic, the grooving of the prism

faces being then especially pronounced. More usually the pyramid and prism faces are about equally developed. Among the smaller individuals, however, crystals of pyramidal habit are fairly common. Single crystals, as a matter of fact, are rare. Even what appear at first sight to be simple forms are generally found to be made up of sub-parallel intergrowths of severe crystals, and complex spear-headed and branching groups made up of a number of such crystals sometimes symmetrically arranged about a central dominant stem crystal are very common. The crystal faces give very poor signals and do not lend themselves to accurate measurement, this applying particularly to those of the unit prism. The only angles which could be determined by means of a Fuess reflecting goniometer with even a fair degree of accuracy were as follows:—

$$oo' = (111) : (111) = 89^{\circ} 24'$$

$$oo'' = (111) : (111) = 52^{\circ} 30'$$

the corresponding values given by Dana<sup>4</sup> being  $89^{\circ} 6'$  and  $53^{\circ} 4'$ .

The crystals are of a very dark olive green colour and their lustre is brilliant. On fractured surfaces the colour is orange brown, the fracture being uneven. The streak is pale canary-yellow. In the process of grinding down the crystals to prepare thin sections an imperfect cleavage parallel to (100) is brought out.

Under the microscope the crystals are seen to have a well-defined zonal structure, being built up of alternations of thick greenish and thinner brown or yellow layers arranged parallel with the faces. These layers are markedly pleochroic, the greenish showing:—

Z = a = pale yellowish-green,

Y = b = pale apple-green,

X = c = very pale yellowish-green,

and the brown or yellow:

Z = a = reddish-brown,

Y = b = greenish yellow,

X = c = pale yellow.

The brownish layers have a much stronger absorption than the greenish. It should be stated that the colours given refer to a fairly thick section. In addition to the brown and greenish zones, a practically colourless zone is generally present in the peripheral portion of the crystals. In one of the sections examined this showed:

Z = pale yellow,

Y = colourless.

<sup>1</sup> According to a valuable unpublished Memorandum by Mr. G. E. B. Froom, Inspector of Mines, South-West Protectorate.

<sup>2</sup> cf. "Die Erzlagerstätten des Otaviberglandes, Deutsch-Südwestafrika," *Metal und Erz.*, XVII., 13, 16, 19, 24, & XVI., 10 & 11.

<sup>3</sup> Schneiderhöhn, *loc. cit.*, p. 33.

<sup>4</sup> "A System of Mineralogy," p. 787.

The precise significance of the zoning is not clear. It may be taken for granted, however, that the differently coloured shells also differ in chemical composition, so that instead of dealing with a homogeneous mineral we have to do with at least three isomorphous substances.

A chemical analysis by Dr. J. McCrae, of some selected crystals is given under I. in the following table:—

	I.	Ia.	II.	III.
PbO .....	55.45	0.25	55.93	54.03
ZnO .....	15.50	0.19	15.94	12.62
CuO .....	3.80	0.05	1.15	8.13
FeO .....	—	—	0.70	—
Fe <sub>2</sub> O <sub>3</sub> .....	0.30	—	—	—
V <sub>2</sub> O <sub>5</sub> .....	22.00	0.12	20.80	22.47
As <sub>2</sub> O <sub>3</sub> .....	Nil.	—	0.32	0.28
P <sub>2</sub> O <sub>5</sub> .....	—	—	0.27	0.17
SiO <sub>2</sub> .....	Nil.	—	0.18	—
H <sub>2</sub> O .....	2.50	0.14	4.37	2.70
H <sub>2</sub> O (110°)	0.05	—	—	—
Total ...	99.60	—	99.82	99.74
Sp. Gr. ....	6.20	—	—	—

Under Ia. are given the molecular proportions corresponding with the analysis. It will be seen that the figures agree fairly closely with the theoretical composition of the mineral, corresponding with the formula 2 PbO. 2(ZnCu) O. V<sub>2</sub>O<sub>5</sub>. 2 H<sub>2</sub>O, according to which lead oxide and zinc plus copper oxide are present in equimolecular proportions, and the ratio of (Pb Zn Cu) O : V<sub>2</sub>O<sub>5</sub> : : 4 : 1. The analyses under II. and III. are adduced for comparison. II. is an analysis by W. F. Hillebrand of descloizite from Beaverbrook, Montana, 0.03 per cent. of CaO and 0.06 per cent. of MgO being present in addition to the constituents named. III. is an analysis of cuprodescloizite from an unnamed locality quoted from Dana.<sup>5</sup> As the term cuprodescloizite appears to be reserved for varieties containing a minimum of 6 per cent. of copper oxide, the Olifantsfontein mineral, which, as we have seen, is probably a complex isomorphous mixture of at least three distinct substances, is best described as cupriferous descloizite.

The associated minerals are pellucid bluish-white quartz and calcite. The latter occurs in mammillary crusts up to 1 centimetre in thickness. In these the calcite is evidently paramorphic after aragonite—a phenomenon also noted at other localities in the Otavi Range.<sup>6</sup> The original aragonite

was clearly of later formation than the descloizite, having been deposited on the crystals of that mineral which project into the crusts. The quartz, on the other hand, appears to be of earlier formation than the descloizite.

*Abenab.*—The Abenab ore is a breccia of strikingly handsome appearance made up of angular fragments of pink surface limestone and reddish dolomite encased by crusts of dark green or brown descloizite crystals, the cementing medium being coarsely crystallised white calcite. The latter forms a network of irregular veins up to 2 centimetres, across which are interspersed with vughs lined with crystals of descloizite and colourless calcite. At least four varieties of descloizite are present, namely:—

(1) A blackish green variety occurring in well-formed pyramidal crystals somewhat elongated in the direction of the macrodiagonal. The prism faces are only very poorly developed, and the habit of the crystals is not unlike that of the descloizite from Lake Valley, New Mexico, shown in Fig. 3, p. 788, of Dana's *Mineralogy*. With the aid of a contact goniometer the following forms were found to be present:—

$$o = 111$$

$$m = 110$$

$$v = 021$$

$$(d) ? = 012$$

On some crystals the faces of the unit prism are bevelled by those of another prism, probably  $l = (1\bar{3}0)$ . On others the edge (111) : (111) is terraced owing to an oscillatory combination of the two clinodromal faces.

(2) A bottle-green variety occurring in smaller crystals of practically the same habit, the prism being, however, even more poorly developed. One peculiar feature of these crystals is that the clinodromal faces often have a peculiar greenish-yellow coating. Whether or not this is due to the alteration of the descloizite is not clear.

(3) A dull greenish-brown variety in which the habit of the crystals is tabular owing apparently to the abnormal development of the macropinacoid, the other forms present being the unit pyramid and the unit prism.

(4) A lustrous chrome-brown variety occurring mostly in peculiar parallel-growth aggregates, up to 1.5 centimetres in length, imbedded in white calcite. The aggregates are due to the regular conjunction of small crystals of pyramidal

<sup>5</sup> "A System of Mineralogy," p. 789.

<sup>6</sup> cf. Schneiderhöhn, loc. cit., p. 41.

habit and are terminated by the unit pyramid. Some of them are doubly terminated.

Chemically the several varieties enumerated appear to differ mainly as regards their copper content. The bright chrome-brown variety is practically free from that element, whereas the very dark variety contains fair quantities of it. No analysis of any particular variety is available, but a sample of the concentrate obtained by jigging the crushed ore, in which all of them are probably represented, showed:—

PbO = 51.81 per cent.

ZnO = 18.06 "

CuO = 1.10 "

V<sub>2</sub>O<sub>5</sub> = 20.60 "

P<sub>2</sub>O<sub>5</sub> = 0.08 "

The writer's thanks are due to Dr. F. E. Wright and Professor Charles Palache for assistance in his investigations.

(From "The South African Journal of Science," Vol. XIX., 142-145.)

#### ROYAL INSTITUTION OF GREAT BRITAIN.

WEEKLY EVENING MEETING, FRIDAY, MAY  
4, 1923.

SIR JAMES CRICHTON-BROWNE, M.D., LL.D.,  
F.R.S., TREASURER AND VICE-PRESIDENT,  
IN THE CHAIR.

#### THE ORIGINS OF THE CONCEPTION OF ISOTOPES.

A Lecture delivered by Frederick Soddy,  
M.A., F.R.S.

(Continued from Page 95.)

Similarly, the chemical identity of radium D and lead was established as a consequence of very prolonged and refined chemical examination. Paneth and Hevesy established upon this their well-known method of using radioactive isotopes as indicators for elements in too small quantity to be dealt with except by such methods. On the principle that wherever the radioactive element is there will its inactive isotope be also, provided that they have once been properly mixed, many difficult or uncertain chemical analyses may be converted into simple radioactive ones.

In 1909 Strömholm and Svedberg made

what was probably the first attempt to fit a part of the disintegration series into the Periodic Table, and although the effort in itself was in an important respect erroneous, in their paper is to be found the first anticipation that the chemical non-separability found for certain pairs and groups of radio-elements may also apply to the non-radioactive elements. Remarking on the fact that there are three parallel and independent radioactive series, they suppose this to proceed down through the Periodic Table, "but that always the three elements of the different genetic series, which thus together occupy one place in the periodic system, are so alike that they always occur together, and also have not been able to be appreciably separated in the laboratory." They point out also this idea would explain the exceptions to the periodic system "if the elements of the scheme were mixtures of several homogeneous elements of similar but not completely identical atomic weight."

In the next year I arrived independently, and without in the least postulating any continuance of the genetic series beyond the radio-elements, at a similar view. Marcwald and I found independently that mesothorium I was chemically similar to radium, a fact undoubtedly known to Hahn and those engaged in the technical extraction of mesothorium, but kept secret. It was known from some work of Boltwood that precipitating barium sulphate in a solution containing mesothorium removes it, but it was thought that the action of the barium sulphate was similar to that in removing uranium X, for which it had long been used—namely, a simple adsorption. I was surprised to find it absolutely different. The removal of the barium from the mesothorium, as from radium, could only be accomplished by the fractional crystallisation of the chlorides. In this fractionation the radium and mesothorium remained together and behaved as a single element. Within the limit of error of the most careful radioactive measurements, there was no change in the relative proportion of the two elements at the end of the process, from that in which they exist in the original mineral. Chemistry has many cases of elements similar in chemical character, but nothing approaching this. For we know, beforehand, that we are dealing with a mixture of two substances, and can estimate accurately the proportion of each individual. Yet to all chemical operations they behave as a

single substance. The differences of atomic weight are considerable, two units in the cases of mesothorium and radium, and of ionium and thorium, and four units in that of radiothorium and thorium. It was certain that if isotopes existed in the case of the ordinary chemical elements, the absence of a second radioactive nature independent of the chemical nature would make it impossible for them to have been recognised. Hence the implication followed that any supposed element may be a mixture of several chemical identities of different atomic weight, and any atomic weight might be merely a mean number (Ann. Reports, Chem. Soc., 1910, 286). There is an element of tragedy in this. The life-time labours of the chemists who, since the time of Stas, have devoted themselves to the exact determination of atomic weight, appear to have as little theoretical interest now, as if you sought to determine the average weight of a collection of beer bottles, all exactly alike, but not all quite full.

#### THE RADIO-ELEMENTS AND THE PERIODIC LAW.

The years from 1911-1913 were crowded with important advances, and to do the exact history justice would take an undue share of the available time. In 1911 the chemistry of most of the  $\alpha$ -ray giving members were sufficiently known for it to be seen that the expulsion of the  $\alpha$ -particle caused the element expelling it to move from the place it occupied in the Periodic Table to the next place but one to it in the direction of diminishing mass.

At this time the chemistry of the post-emanation members had scarcely been studied, though von Lerch, from electrochemical researches, had put forward the rule that the successive products are each electrochemically "nobler" than the last, a rule which describes well enough the electrochemical behaviour of the first three—the A to C members, as they are called. Then as a result of the experiments of Schrader and Russell, it was found that their volatility was much affected by chemical treatment and by the atmosphere in which they were volatilised. Thus, in hydrogen, radium C volatilises at as low a temperature as 360° C., though, in air, a temperature of 1200° C. is necessary. This clearly indicated the possibility that even these excessively ephemeral elements have a definite chemical character. Hevesy showed, by electrochemical methods, that

the three B-members are identical in properties among themselves, and also the three C-members.

But the work, which, more than anything else, served to reveal as in a flash the simple and sweeping generalisation which covers the evolution of the radioactive elements was that of A. Fleck in my laboratory in Glasgow. He studied the chemistry of the various members, still uncharacterised, from the definite point of view of ascertaining to which element each most closely approximated in chemical character, and then whether it was separable from that element or not. In addition to confirming more rigorously many conclusions already reached, he proved that mesothorium 2 was non-separable from actinium, the three B-members from lead, like radium D, and the three C-members and radium E from bismuth.

Hevesy and Russell—the first with regard to the valency of the radio-elements and the second with regard to the positions they occupy in the Periodic Table—published early in 1913 statements of the full law underlying radioactive evolution, but only in part correct. Within a month, K. Fajans in Karlsruhe published the scheme correct and complete, including the complicated branchings that occur at the C-members. In a paper, amplifying and amending Russell's scheme, I arrived independently at the same place as Fajans. Each  $\alpha$ -ray expelled causes a shift of two places in the Periodic Table in the direction of diminishing mass, and each  $\beta$ -ray a shift of one place in the opposite direction. In its present form the scheme is shown in the figure. The chief uncertainty remaining is whether the actinium branch starts from uranium II, as shown in the figure for convenience, or from uranium I, or even from a third independent isotope of uranium. So that the atomic weights shown for the actinium series are purely provisional.

By the consistent application of the two rules mentioned the members found to be non-separable from one another fall in the same place in the Periodic Table. The chemical character has nothing to do with the radioactivity, nor with the series to which the element belongs, nor with its atomic weight. It depends upon a number, now called the atomic number, shown at the top of the place in the figure.

Before passing on to this, the chief practical consequences of the generalisation





ment showed that scattering was approximately proportional to the square of the atomic weight. So that it looked as if, as in the  $\alpha$ -particle itself, there existed one unit of nuclear charge to each two units of atomic weight. This would make the nuclear charge of uranium, of atomic weight about 240, 120 +.

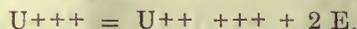
Since the  $\alpha$ -particle carries two positive charges and the  $\beta$ -particle one negative, the obvious inference from the figure is that the successive places in the Periodic Table correspond with unit difference in the intra-atomic charge. This view, and also that each unit of charge corresponded to two units of mass, had been suggested independently by van der Broek in 1911. At first he tried to stretch the Periodic Table to make it accommodate 120 places. But, in 1913, he pointed out that the experimental results for scattering were completely in accord with his own view (that the number of the place is the same as the intra-atomic charge), on the existing Periodic Table, which accommodates only some 90 elements. It would not be inconsistent with his other view (that the nuclei of the heavy elements are made up of helium nuclei) if there were electrons in the nucleus as well as in the outside shell. Thus uranium in the 90th place would have to have, in addition to the 60 helium nuclei in its nucleus to account for its weight, 30 electrons, to account for its charge of 90+.

The existence of electrons as well as positive charges in the atomic nucleus was also postulated by Bohr to explain the emission of  $\beta$ -rays, for on his theory the electrons in the external shell form a stable configuration and could only be dislodged by the expenditure of work.

The Periodic Law generalisation practically settled this question.  $\beta$ -ray changes are no less transmutational than  $\alpha$ -ray changes, and are shanply to be distinguished from the numerous processes, such as friction, chemical change, action of ultra-violet light and incandescence, during which electrons are detached from atoms. The effect on the chemical character produced by the expulsion of one  $\alpha$ -particle is exactly undone by the expulsion of two  $\beta$ -particles, and the product becomes isotopic with the original parent. This means that both  $\alpha$ - and  $\beta$ -particles must be expelled from the nucleus, and that isotopes are elements the atoms of which have the same *nett* nuclear charge—*i.e.*, the same excess number of positive over negative charges in the nucleus, but different numbers of positives and negatives reckoned separately. For such systems the

electronic shell would be identical, and so the identity of the chemical and spectroscopic character is explained. Also the atomic volume is the same—that is, the density must be proportional to the atomic weight.

We were able to get an interesting confirmation of this view. In the change of uranium X<sub>1</sub> to uranium II two electrons are lost as  $\beta$ -rays. In the oxidation of a uranous salt to a uranic or uranyl salt two electrons are also lost.



If these come from the same region of the atom as the  $\beta$ -particles, then uranous salts, so long as their valency does not change, should be like uranium X<sub>1</sub>, chemically non-separable from thorium. Fleck, trying this, found great similarity in chemical properties between uranous salts and thorium, but not identity. He was able to separate them by chemical methods without changing the valency of the uranous salt.

The great merit of the nuclear atom from the chemist's point of view was that it afforded for the first time a clear picture of the difference between a chemical and a transmutational (or radioactive) change. The latter occur in the nucleus and are irreversible. The external shell accommodates itself instantly to the change of the nucleus. But any change suffered by the external shell (chemical change) has no effect on the nucleus, which always acts so as to make the external shell conform to one most stable configuration.

The atom is an *imperium in imperio*, and like most such systems is very conservative and resistant to change. The electrons in the shell, that govern almost all the atomic properties, except mass and radioactivity, are in turn but the bureaucratic instruments of the real government, which is the intensely charged central nucleus. The transmutation of atoms, as of social systems, is alike impossible because the apparent government is not the real government. Rutherford's experiments, on the bombardment of atoms by  $\alpha$ -particles, show that only about one out of a hundred thousand of the latter in passing through hydrogen ever hit a hydrogen nucleus, and the proportion of hits to misses is something like one in one thousand millions. In politics, contrasting the number of missiles hurled with the results achieved, the shooting seems even worse. It is only when the atomic or social systems break up or break down that we learn even of the existence of their real internal constitution.

F.S.

## GENERAL NOTES

THE BRITISH INDUSTRIES FAIR,  
1924.CONSIDERATIONS GOVERNING THE CHANGE  
OF DATE.

After considering all sides of the question and canvassing interested trade opinion, the Department of Overseas Trade and the Birmingham Committee, the respective organising authorities for the London and Birmingham sections of the British Industries Fair, have decided that next year's Fair, instead of taking place at the end of February, as would normally be the case, shall be postponed for two months.

This means that the British Industries Fair will open in London on April 28, continuing until May 9, while the Birmingham section will open on the Monday following the close of the Fair in London.

## VISITORS FROM THE DOMINIONS.

In selecting these dates the organising authorities appreciated that the holding of the big British Empire Exhibition from April to October of 1924 must materially affect the attendance of overseas buyers. It is certain that few buyers from the Dominions will make two visits to the United Kingdom in the course of a single year, as would be necessary if the Fair were to be held two months before the opening of the Empire Exhibition. On the other hand, it is probable that many of these visitors will make a point of arriving in this country in time for the opening at Wembley, a probability which becomes almost a certainty if they can, in the course of the trip, inspect both the Exhibiton and the British Industries Fair.

The later date is also likely to benefit the Fair owing to the probable large increase in the number of Dominions business men who will make every possible effort to come to the United Kingdom next year. Nor need it be considered that this increase of visitors will be limited to the Dominions and Colonies; so large an exhibition as that of the British Empire promises to be, is a magnet to both the business man and the holiday-maker. With the Fair running concurrently with the Exhibition, many Continental buyers will assuredly seize the opportunity of combining business with pleasure by visiting this country in May next.

## EXHIBITION AND FAIR COMPLEMENTARY.

While the British Industries Fair and the

British Empire Exhibiton have a common object in the promotion of Empire trade, their activities are complementary rather than competitive. Participation in the Fair will, as always, be confined to British manufacturers, and admission will be restricted to trade buyers. The exhibition, on the other hand, is for the public, and welcomes participation by any British firm, whether manufacturers, merchants or retailers.

Mutual benefit to both the Exhibition and the Fair will also be possible from a combined publicity campaign.

## TRADES TO BE EXHIBITED.

The schedules of trades for the London and Birmingham sections of the Fair will be similar to those of last year, London covering mainly the lighter lines of goods such as pottery, jewellery, leather and fancy goods, sports goods, musical instruments, stationery and chemicals, while exhibits at Birmingham will consist of hardware, engineering, metals, power, building, mining and agricultural implements.

Application forms for space will be issued to eligible United Kingdom firms at the beginning of October.

Since this general statement was written many replies have been received by the Department of Overseas Trade to their circular regarding the change of date. It is satisfactory to record that the vast majority of these express not only the intention of the various firms to exhibit, but also universal approval to the decision to alter the dates in the special circumstances ruling next year.

NEW POWER SCHEME FOR  
JOHANNESBURG.

H.M. Senior Trade Commissioner in South Africa reports that the Johannesburg Town Council has now voted in favour of the proposed new power station and advises its erection on the vacant site between the present power station and Jeppe Street. It also recommended that, in the period which must elapse before the new power station is completed, a 10,000 kilowatt generator, adaptable to the new conditions, should be installed in the old power station on temporary foundations, to be afterwards removed to its permanent position in the new station, and that the matter should be treated as urgent in order to have the set running before the winter of 1925.

The total cost of the new station will be

about £500,000; it will be equipped with two 10,000 k.w. generators, together with two generators from the old station, so as to give a capacity of 39,000 k.w.

The Finance Committee has also recommended the erection of this power station, provided that authority is obtained from the Administrator to borrow an amount of £525,000.

Copies of press cuttings in connection with this matter may be inspected by United Kingdom firms interested on application to the Department of Overseas Trade (Room 52), 35, Old Queen Street, London, S.W.1. (Reference No. 11670/E.D./E.P.)

#### IN PARLIAMENT.

In the House of Commons, Mr. Shinwell asked the President of the Board of Trade whether he was aware that sulphate of ammonia for export from the Clyde was not being weighed and checked, and that sealed samples were no longer taken; and whether, since this was contrary to custom, he proposed to take action in the matter.

Viscount Wolmer, Under-Secretary to the Board of Trade, said: The official control of the export of sulphate of ammonia, which was instituted during the war, is now at an end. The export is, accordingly, subject only to the ordinary Customs regulations, and I have no reason to think that these regulations are not being observed. The hon. member appears to be referring to certain trade arrangements, over which the Board of Trade have no control.

Mr. Herbert Spencer asked the President of the Board of Trade whether his attention had been called to the statement of the President of the Colour Users' Association to the Manchester Chamber of Commerce of 23rd February, 1923, in which he asked the Government to redeem its pledge that the Act should not jeopardise the using industries; and whether the Government did propose to do so; further, whether his attention had been called to the statement of the President of the Colour Users' Association that prices both of home-produced and reparation dyestuffs were at an artificially high level, 300 to 400 per cent. above pre-war; and what steps he proposed to take to remedy this.

Sir Philip Lloyd-Greame replied: I am in constant communication with the representatives of the dye-making and dye-using ind-

ustries, and every effort is being made to secure that the Dyestuffs (Import Regulation) Act is administered in such a manner as to promote the best interests of both parties.

In a lecture recently given by Evan James McGillivray, at the Institute of Chemistry, some interesting points are raised as to the right to use the title "Chemist."

Mr. McGillivray made some extracts from Dr. Spratt's "History of the Royal Society," written in the 17th century, where it is suggested that the chemist "must be rather innocent and virtuous than knowing"—qualifications that are well worth bearing in mind.

According to Dr. Spratt, chemists of his day might be divided into three ranks—

"Such as look after the knowledge of Nature in general."

"Such as seek out and prepare medicines."

"Such as seek after riches by transmutations and the great Elixir."

The lecturer suggested that those who composed the Chemical Society at the time of its foundation were the successors of the men to whom Dr. Spratt refers as those "who look after the knowledge of Nature in general," and that they were very little known to the general public.

Of the other two ranks, the pharmaceutical chemist is still known to the public as a chemist, while those who sought after riches by transmutations and the great Elixir have disappeared—killed by ridicule and failure.

We have received a copy of the Index to Vol. I. of the Bureau of Bio-Technology, and are asked to make it known that it may be obtained on application to Messrs. Murphy & Son, Ltd., Cedars Laboratories, Sheen Lane, Mortlake, London, S.W.14.

#### DEPARTMENT OF OVERSEAS TRADE.

REPORT ON HIS MAJESTY'S TRADE COMMISSIONER AT TORONTO IN REGARD TO AN OFFICIAL TOUR OF WESTERN ONTARIO; JUNE, 1923.

An official tour was made by His Majesty's Trade Commissioner at Toronto (Mr. F. W. Field) to cities and towns in Western Ontario during the early part of

May and the latter end of June. Among the places visited were Hamilton, St. Catharines, Niagara Falls, Thorold, Brantford, London, Chatham, Stratford, Windsor, Walkerville, Ford, Amberstburg, and Ojibway.

A large number of calls were made upon manufacturers, who are importers of various commodities, merchants, and others likely to be interested in sources of supply in the United Kingdom.

These official tours, which are a part of the duties of all of His Majesty's Trade Commissioners, are believed to be of considerable value in relation to the expansion of British trade. In the case under review, contact was established or maintained with Chambers of Commerce, Industrial Commissioners, Purchasing Agents, and others interested. The Trade Commissioner reports that business men in Ontario generally appreciate the work of the Department of Overseas Trade in assisting to develop British trade here in face of keen foreign competition. He adds that he is always given a friendly reception and every possible assistance. Considerable publicity in the interests of British trade was also secured through press interviews at the various points visited.

Enquiries were received by the Trade Commissioner during his tour for prices of United Kingdom manufacturers of yarns, dyeing machinery, alloy steels, wire drawing machinery, paper tubes, vegetable parchment paper, fluospar, duck filter cloth, soda ash, etc. These were brought to the notice of United Kingdom firms. A recent enquiry of this character has led to an important new connection or United Kingdom chemical manufacturers.

#### SILK DYEING.

A visit was made to the silk dyeing works which were recently established in St. Catharines, Ontario, where it was learned that a considerable volume of silk goods in the grey are being imported from foreign countries and dyed locally. A special report on this matter is available to firms interested upon application to the Department of Overseas Trade.

#### AMERICAN BRANCH WORKS.

American companies continue to erect branch works in Western Ontario. Two of the most recent additions are the United States Light and Heat Company and the Dominion Insulator and Manufacturing Co. The latter firm are one of two insulator manufacturers in Ontario which specialise

in high voltage work. Clay is imported from the parent company prepared ready for use in the Canadian works.

The establishment in Canada of so many branch works of United States firms naturally tends to divert trade to the United States. Many of the Canadian branches purchase a substantial portion of their requirements through their head office in the United States which in some cases entirely controls the purchasing policy of the Canadian branch. Production costs in Ontario are frequently reported as being higher than in the parent works in the United States.

#### AMERICAN CAPITAL IN CANADA.

It was recently estimated by a reliable authority that more than two hundred branch factories were opened in Canada by Americans in 1919, and a great number in 1920 and 1921, and that late in 1922 there must have been over seven hundred such establishments, with a further number seeking suitable locations. One of the incentives for this development is that the American manufacturers can thus supply the Canadian market and at the same time escape the Canadian tariff. Another is that by manufacturing in Canada they are able to enjoy the preferential treatment accorded to Canadian goods by many countries within the British Empire, while, under the terms of an agreement with France existing since 1907, Canada's products enter that country under especially favourable conditions.

#### BRITISH BRANCH WORKS.

A number of United Kingdom manufacturers are believed to be considering the matter of branch works in Canada, particularly in Ontario and Quebec Provinces. These include makers of artificial silk yarn and engineering lines. An English firm of tobacco merchants recently established processing works in Ontario.

#### CHEMICAL INDUSTRIES.

The Norton Company proposes to enlarge its electric furnace plant at Chippewa, near Niagara Falls, by adding a furnace building to be used exclusively for the manufacture of a carbide of silicon abrasive known as Crystolon. The development will cost about \$165,000, and ensure a 25 per cent. increase in production of this line.

There are two cities bearing the name of Niagara Falls. One is in Ontario and one in New York State. They face each other, the river dividing them. Both are the sites of important industries. The Falls themselves are just as much a Canadian institution as

they are American, and the famous "Horse-shoe Falls" of Niagara are in Canada. Power is developed at Niagara Falls, Ontario, by the Hydro-Electric Power Commission of Ontario for long distance transmission to all parts of Ontario and to several parts of new York State.

The American Cynamid Company have works at Niagara Falls, where the company's output is equally divided between cynamid, one of the raw materials of fertiliser, and cyanide, used in mining. The mining industry has shown marked improvement, with the result that sales of cyanide have been made to the gold mines in the South African Rand as well as in Canada, the United States and Mexico.

#### BUSINESS CONDITIONS.

Business conditions in Western Ontario still leave something to be desired, but they are gradually improving. The iron and steel industries have recently been more active, largely as a result of orders placed by the railway organisations and by those responsible for bridge and office building construction. Knitted goods, sports clothing, and ladies' clothing manufacturers have also been busy, but men's wear factories have been less active. The demand for machine tools is only fair, but shows improvement. Cotton mills are well occupied. Woollen mills have some idle machinery and complain of active British competition. Chemical makers are experiencing an active demand. Motor car makers are busy.

Wholesale houses report a good demand for staple lines and retail shops are doing a satisfactory seasonable trade.

Collections continue to be reported as difficult.

British manufacturers have made some headway recently in securing a share of Ontario's import trade. This is true of the woollen, hosiery, and chinaware trades particularly. British trade has also been fairly good in fancy leather goods, sporting goods and cloths, chemicals and, to a lesser extent, in metals and machinery.

The competition to be met in Ontario is very keen in the majority of lines, both from Canadian and United States manufacturers. France, Belgium, Sweden, and Japan are also active in certain trades.

#### MACHINERY.

Much machinery of United States manufacture is in use in Ontario factories, and orders continue to be placed there by local buyers. Many factories assist the sales of machinery competing with that of United Kingdom manufacturers. For example, the

majority of Canadian machinists are accustomed to work on American machines, and some difficulty and trouble are experienced in training them to use machines to which they are not accustomed. Operators some times state that they prefer the light-weight machines of our competitors rather than heavier build of British machines, although there is no doubt, as a rule, as to the better finish and durability of British machines. The difficulty in having repairs made without delay and in securing the rapid delivery of spare parts are other reasons operating against larger sales of British machines. The Trade Commissioner expressed the belief that there appears to be an opportunity for increased sales of machinery of various makes in this market, including air compressors, hoisting machinery, mining equipment, textile machinery, and various other lines in which United Kingdom firms have proved specialists. Three of the factors operating against greater business are the lack of sufficient local representation and active salesmanship, the failure of United Kingdom manufacturers to keep in constant touch with those who have purchased their machines, and the inability to effect repairs and supply spare parts at short notice. While the business in any one line may not be large enough to justify the establishment of a proper local organisation, which should remove the difficulties noted, it might prove feasible for several manufacturers of non-competing machinery to have joint representation here, with a technical man to look after repairs; a good sales organisation, which would adopt the American "follow up" system, as it is termed; and a stock of the spare parts which are most likely to be needed. Unless some such system is adopted, it is to be feared that the imports of United Kingdom machinery to this market will become continually smaller.

#### VISITS TO CANADA.

The Trade Commissioner has again strongly recommended a personal visit of United Kingdom manufacturers to the Ontario market in order to appreciate fully the difficulties which United Kingdom manufacturers have to solve in order to secure a profitable amount of the business offering. Indeed, he states that unless the United Kingdom manufacturer is fully conversant with what is termed the "selling atmosphere" of the market, little success is likely to result from efforts to establish or extend trade in that particular market.

The Canadian manager of branch works

of a United Kingdom manufacturer of engineering equipment has suggested that United Kingdom firms establishing works in Canada should consult the Trade Commissioners in regard to other branch houses

there, in order that equipment and supplies may be purchased as far as possible from other United Kingdom firms in Canada, rather than from foreign suppliers.

#### DOMINION BUREAU OF STATISTICS, CANADA.

R. H. COATS, B.A., F.S.S., F.R.C.S.,  
DOMINION STATISTICIAN; S. J. COOK, B.A.,  
A.I.C., CHIEF OF THE MINING METALLURGICAL  
AND CHEMICAL BRANCH.

#### REVISED STATISTICS ON THE MINERAL PRODUCTION OF CANADA, 1922.

No. 1.—COBALT.

*Date of Issue, July 16, 1923.*

The Dominion Bureau of Statistics issues the following finally revised statistics on the production of cobalt in Canada during 1922.

The major portion of the world's supply of cobalt for almost two decades has been derived from the silver-cobalt-nickel arsenides of the Cobalt district.

During 1922, three smelters in Ontario treating ores and residues from this district marketed cobalt oxide, metallic cobalt, cobalt sulphate, cobalt carbonate, cobalt hydroxide, unseparated oxide and stellite (an alloy of cobalt used for high speed tool metal). The cobalt residues from the cyanide process were mainly treated in Canada during 1922, although some of these, as well as smelter residues amounting in all to 518 tons, containing 173,211 lbs. of cobalt, were shipped abroad for treatment.

The cobalt production of Canada in 1922 was 569,960 lbs., which, at \$3.25 per pound, would be worth \$1,852,370. These figures were obtained as the total of the metal cobalt contained in smelter products made in 1922 and cobalt in residues exported for treatment, valued at \$3.25, which was the average New York quotation for cobalt during the year.

#### SUMMARY OF COBALT PRODUCTION STATISTICS, 1922.

Cobalt ores and residues treated or in process, 3,719 tons.  
Metallic cobalt content of the above (by assay), 536,400 lbs.  
Output of Smelters.

	Total lb.	Cobalt Contained lb.	Quantity lb.	Marketed. Value as reported by Smelters. \$
Metallic cobalt .....	106,274	106,274	109,067	282,602
Cobalt oxide .....	360,495	252,347	398,697	798,271
Mixed oxide .....	86,730	39,023	123,605	99,687
Residues exported .....	A	172,311	1,036,000	156,402B
Total .....	Quantity Computed value	569,960	.....	1,336,962
		1,852,370		

A — Not given; B — Estimated.

#### NOTICES OF BOOKS.

*The Discovery of the Nature of the Air and of its Changes during Breathing*, by CLARA M. TAYLOR, M.A. Geo. Bell & Sons, Ltd., London. 1923. Price 1s. 6d. net.

This work forms part of a series of classics of scientific method edited by E. R. Thomas, M.A., M.Sc., Headmaster of the Royal Grammar School, Newcastle-on-Tyne, and the object of the series is to provide reproductions of the great masterpieces of

science in convenient form, together with an account of the action and reaction of ideas which, through the process of time, led up to the crucial experiments carried out and described by some great master, and the hope is expressed that a reader taking up a volume of the series dealing with a branch of science of which he is ignorant will be able, without further help, to trace the steps by which the human mind has passed from chaotic ignorance to ordered knowledge.

The volume in question contains eight

chapters referring to researches from those of Robert Boyle in 1627-1691 to those of Lavoisier in 1743-1794. A great many illustrations and portraits are given of the men whose works are described, and many details are recorded of the work of these early investigators that it would be difficult for the ordinary student to obtain. The book is written in a style that it is very easy to follow. At the end of each chapter there is a short summary giving the dates of the investigations and the evidence they obtained.

A great many of the memoirs referred to are quoted in full, particularly that of Lavoisier on the respiration of animals and the changes which occur in air as it passes through the lungs.

The book ends with a summary of the progress in knowledge of respiration, commencing with Harvey's discovery of the circulation of the blood in 1678 to the work of Lavoisier in 1743.

#### BOOKS RECEIVED.

*The Paper-Makers' Directory of All Nations.* Pp. XLIX. + 971. Thirty-Second Edition, 1923. Messrs. Dean & Son, Ltd., Debrett House, 29, King Street, Covent Garden, W.C.2. Price 21s.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 19218—Kenkel et Cie.—Treatment of ammonium chloride lyes in iron vessels. July 26.  
 19299—Michael & Co., J.—Manufacture of nitrate of potassium. July 27.  
 18944—Pratt, J. T.—Desulphurising iron, steel, and ferro-alloys. July 24.  
*Specifications Published this Week.*  
 17528—Posseyer Abwasser-und-Wasserreini-Gungs Ges. E.—Removal of phenol and its homologues from waste waters.  
 178824—Metz, H. A.—Complex arseno-stibino compounds and process of making the same.  
 200760—Koppers Co.—Recovery of alkali thiosulphates from solutions.

- 200151—Howards & Sons, Ltd., and Blagden, J. W.—Manufacture of thymol.  
 200160—Plauson's (Parent Co.), Ltd.—Manufacture of cellulose derivatives and fibrous products.  
 200167—Adam, W. G., Siderfin, N. E., Murdoch, D. G., and Galbraith, W. L.—Chemical reduction of organic compounds.  
 200176—Spensley, J. W., and Chemical Engineering Co. (Manchester), Ltd.—Production, mixing, blending, or refining of food products containing fats  
 200186—Zdanowich, J. O.—Manufacture of cellulose acetates.

#### Abstract Published this Week.

- 198829—Pyrazolone derivative; dyes. — Soc. of Chemical Industry in Basle, Switzerland.

1-(2-Methyl-3-sulpho-5-isopropyl) phenyl-3-methyl-5-pyrazolone is prepared by condensing the hydrazine from 2-aminocymene-6-sulphonic acid with ethyl acetoacetate. An example is given in which diazotized aminocymene sulphonic acid is reduced with sulphite and the hydrazine then condensed with ethyl acetoacetate.

Monoazodyes which dye wool in yellow shades similar to those of tartrazine but faster to light are obtained by coupling the above described pyrazolone derivative with diazo compounds of the benzene or naphthalene series; in an example diazo-benzene is used.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

#### UNIVERSITY OF MANCHESTER.

#### CHEMISTRY COURSES.

A PROSPECTUS containing full particulars of the Lectures and Laboratory Courses qualifying for Degrees in Chemistry will be forwarded on application to the Internal Registrar.

The Session Commences on October 4th. Applications for admission to the Research Laboratories should be made to the Director of the Chemical Laboratories.

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## THE CHEMICAL NEWS,

VOL. CXXVII. No. 3306.

## ORGANIC COMPOUNDS OF ARSENIC.

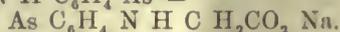
## PART IIIA.

By R. F. HUNTER, F.C.S.

## SALVARSAN.

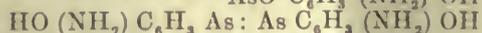
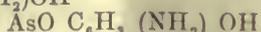
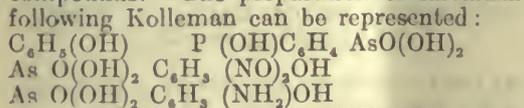
The high physiological activity of the cacodyl compounds is traced to the presence of trivalent arsenic. This led Erlick to study the trivalent arsenic compounds which are generally obtained by reducing the corresponding atoxyls.

A drug of high trypan ocidal power is "Spirarsyl," and has a constitution  $\text{CO}_2 \text{Na CH}_2 \text{N H C}_6\text{H}_4 \text{As} =$



and is much less toxic than atoxyl.

The work that has been done on this subject (I refer to salvarsan) at first sight, appears overwhelming, and no attempt can be made to give anything like a complete survey of the work. The suggestion is, then, to follow Morgan's classification, and to consider a few of the more important compounds. The preparation of salvarsan following Kollman can be represented:



1.—Reduction products of p-hydroxyphenyl arsenic acid and derivatives:

These we can enunciate briefly as  
p-hydroxy phenyl arsenious oxide;  
p-arsenophenol;

Tetra chlorarsenophenol;

and arsenobenzene is H oxymethylene carboxylic acid

$\text{CO}_2\text{H CH}_2\text{O O}_6\text{H}_4\text{As As C}_6\text{H}_4\text{O CH}_2\text{CO}_2\text{H}$ , which found great use in case of animals infected with trypanosomes.

2.—Amino aryl derivatives which contain trivalent arsenic:

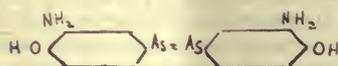
p-Amino phenyl arsenious oxide,  $\text{NH}_2\text{C}_6\text{H}_4\text{As 2H}_2\text{O}$ , is prepared by reducing atoxyl with  $\text{SO}_2$  and HI.

Derivatives worthy of note are:

2-Aminotolyl-5-arsenious oxide 2-acetyl amino 1:5-benzarsenious conde.

3.—Salvarsan:

3: 3' Diamine 4: 4' dehydroxy arsenobenzene



Commercially the compound is generally used as its hydrochloride.

Commercial samples contain impurities, and in some recent investigations King isolated a number of sulphur compounds from the commercial salt (*J.C.S.*, 1921).

The solution of salvarsan in water is acid, and it is necessary to neutralise this acidity previous to injection, one of the disadvantages of salvarsan. As a derivative of arsenobenzene, salvarsan is exceedingly readily oxidised by air. This is important because the product of oxidation is 3-amine-4-hydroxyphenyl arsenious oxide, which is very much more toxic than salvarsan.

Sodium salvarsan has been much used in venereal work.

Copper salvarsan in sleeping sickness: Methylation of salvarsan decreases its healing powers.

## 4.—Isomerides of salvarsan:

The medicinal value of the isomerides is in all cases less than that of salvarsan. The following isomerides have been prepared:

4: 4' diamino.

3: 3' dehydroxy arsenobenzene

2: 2' ..... 2: 2' .....

2: 2' ..... 5: 5' .....

and 4: 4' ..... 2: 2' .....

5.—Derivatives and homologues of salvarsan:

Some of these are worthy of mention.

3-Methylamino-4-hydroxy phenyl arsenic acid. Sym. 3:3' dimethylamino 4:4' dehydroxy arsenobenzene.

3-Dimethylamino-4-hydroxy phenylarsenic acid are examples of N. methyl derivatives, while

3 3' diamino 2 2' dehydroxy 5 5' arsenotoluene 4 4' diamino 5 5' dehydroxy 2 2' arsenotoluene are examples of C methyl derivatives.

5 5' dichloro 4: 4' diamino 3 3' dehydroxy arsenobenzene 4 4' diamino  $\alpha$ -arsenonaphthalene and 3: 3' diamino 4 4' dehydroxy  $\alpha$ -arsenonaphthalene have been prepared.

Stilbene analogues such as

5: 5' diamino 2: 2' stilbene 1: 1' diarsenic acid 5: 5' diamino 4: 4' dehydroxy 1: 1' arsenic 2: 2' stilbene, are known.

Also the mixed aromatic-aliphatic cacodyl analogue of salvarsan, viz., 3: 3' diamino 4: 4' dehydroxy diphenyl dimethyl diarsine has been prepared.

## 6.—Tetraminoarsenobenzenes:

Among the reduction products of 2:4 dinitro phenylarsenic acid we might mention 2:4 Dinitro phenylarsenious oxide, and 2:4, 2':4' Tetranitro arsenobenzene.

## 7.—5:5' Diamino 2:4 : 2' 4' tetra hydroxy arseno benzene and derivatives:

Among the preparations which have been carried out are those of

2:4 Dihydroxy phenyl arsenic acid and 5:5' Diamino 2:2' dimethoxy 4:4' dehydroxy arsenobenzene.

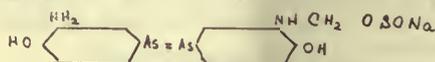
## 8.—Hexamino arsenobenzene and derivatives:

4:4' Tetramethyl 3:4 : 5 : 3' : 4' : 5' hexaminoarseno benzene is said to be a promising trivalent arsenic compound.

## PART IIIb.

## NEO SALVARSAN:

Sodium 3:3' Diamino 4:4' dehydroxy arsenobenzene. N. Methylene sulphinate

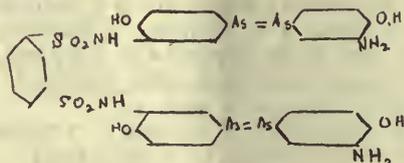


Neo salvarsan is prepared from salvarsan hydrochloride by treatment with sodium formaldehyde sulphoxylate in aqueous solution, followed by 10 per cent.  $\text{Na}_2\text{CO}_3$  when 3:3' diamino 4:4' dehydroxy arsenobenzene N. methylene sulphonic acid precipitates from which the sodium salt, neo salvarsan, can be obtained.

Neo salvarsan is neutral in solution; its curative effect is much the same as salvarsan, but greater doses must be applied.

2.—Galyl 4:4' dehydroxy arsenobenzene 3:3' phosphamic acid is an arsenical drug which is acidic and dissolves in aqueous  $\text{Na}_2\text{CO}_3$  to a neutral solution and is very suitable for intravenous injection in treatment of syphilis.

Ludyl or benzene m 3':3' disulphamino bis 3 amino 4:4' dehydroxy arsenobenzene is also used in syphilis, and has a structure



3.—Arsenoarylglycines, an example of which is arseno phenyl p glycine,  
 $\text{CO}_2\text{HCH}_2\text{NH C}_6\text{H}_4\text{As}$ :  
 $\text{As C}_6\text{H}_4\text{NHCH}_2\text{CO}_2\text{H}$

the sodium salt of which is "spirasyll." Arsenohippuric acid has recently been prepared and has a constitution  
 $\text{CO}_2\text{HCH}_2\text{NHCHOC}_6\text{H}_4\text{As}$ :

$\text{As C}_6\text{H}_4\text{CO NHCH}_2\text{CO}_2\text{H}$ .

In conclusion, we have surveyed in an infinitesimally small way the work which has been done on arsenic organic compounds.

That the ultimate cure for syphilis, the worst of the two venereal diseases, will be an arsenic aromatic or hetero cyclic, there can be little doubt; when we consider that in 1918 the figures given for British troops suffering from venereal disease amounted to 200,000, we get a vague conception of the magnitude of the vital problem of arsenic organic derivatives. From the brilliant work done by our scientific men in this field of research, we are sanguine enough to hope that in a few years' time we shall see the advent of a cure, better by far than either neo salvarsan or its derivatives, if not the absolute cure for that filthy and contagious disease, once unknown in this country, now having spread and spreading to a ghastly degree, which we call "syphilis" by name.

### NOTES ON THE QUANTITY AND PROPERTIES OF CHARCOAL OBTAINED FROM VARIOUS KINDS OF SIAMESE WOODS.

By DR. G. BOSSONI, ROYAL NAVAL ORDNANCE DEPARTMENT, BANG NA (SIAM).

March, 1923.

It is well known how great is the importance of charcoal in the manufacture of black powder, and how the quality and properties of charcoal are intimately connected with the quality and properties of black powder.

In fact, the combustion of black powder depends in great part on the facility and rapidity of the combustion of charcoal, therefore before proceeding to the manufacture of black powder, it is necessary to study the properties of the charcoal which enters into the composition of the powder. For this purpose, Section IV. of the R. Siamese Naval Ordnance Dept. has undertaken some experiments on the quality and quantity of charcoal yielded by several kinds of common Siamese woods, and as the yield of charcoal depends not only upon the kind of wood, but also upon the manner of charring employed, so the experiments were rigor-

ously performed under the same conditions and at the same temperature (350° C.) for all the woods.

The wood was cut from trees approximately three years old during the dry season, and the branches not more than 4 centimetres thick, about 50 centimetres long, were stripped of the bark and then charred.

Table No. 1 shows the various kinds of woods in the order of their yield of charcoal, together with the specific gravity of the charcoal.

Table No. 2 shows the results obtained from the analysis of charcoal residue in the still, per cent.

As the charcoal most suitable for the manufacture of gun powder is the one which burns most quickly and gives the least quantity of ash, experiments were undertaken to determine the rate of combustion of the various kinds of charcoal, according to the Proust's method. A mixture of 0.645

grammes of saltpetre to 0.130 gramme of charcoal was placed in copper tubes 6 centimetres long and 6 millimetres in diameter, and ignited by a little meal powder. Table No. 3 shows the results obtained.

In conclusion, from the above experiments it appears that although the quantity of charcoal obtained from 100 parts of Mai Makham Teth (*Pithecolobium dulce*), and Mai Kaa (*Sesbania grandiflora*) is higher than the quantity yielded by the other woods, the charcoals obtained from Mai Thonglang (*Erythrina indica*) and Mai Tinpet (*Alstonia scholaris*) is richer in carbonium and burns more quickly.

I wish to take this opportunity of expressing my thanks to Dr. F. G. Kerr, of the Botanical Section, Dept. of Commerce, and Mr. W. F. Lloyd, Conservator of Forests, for informations with regard to the botanical names of trees.

TABLE NO. 1.

	DRYING.		Loss.		CHARRING.			
	Weight of the wood.				Weight of the wood dried previously at 100° C.	Quantity of charcoal obtained from 100 parts of wood.	Specific Gravity of charcoal.	
	Before drying.	After drying.	Off weight of dry wood	Per cent.				Before charring.
Mai Makham Teth ( <i>Pithecolobium dulce</i> ) .....	25.00	15.97	9.03	36.12	15.97	6.06	37.94	1.74
Mai Kaa ( <i>Sesbania grandiflora</i> ) ....	22.00	19.27	2.73	12.40	19.27	7.09	36.79	1.318
Mai Pho Tale ( <i>Hibiscus Tiliaceus</i> )	18.00	16.14	1.86	10.33	16.14	5.43	33.64	1.31
Mai Tinpet ( <i>Alstonia scholaris</i> ) ....	22.50	12.35	8.15	39.75	12.35	3.49	28.25	1.47
Mai Thonglang ( <i>Erythrina indica</i> )	25.00	22.80	2.20	8.80	22.80	5.29	23.20	1.75
Mai Lampoo ( <i>Sonneratia acida</i> ) ...	20.00	9.24	10.76	53.80	9.24	2.18	23.59	1.57

TABLE No. 2.

Analysis of Charcoal obtained from	Carbon.	Oxygen.	Hydrogen.	Nitrogen.	Ashes.
Pithecolobium dulce .....	78.10	16.50	3.67	Traces	1.60
Sesbania grandiflora. ....	77.90	16.40	3.75	do.	1.85
Hibiscus tiliaceus .....	77.02	17.00	3.70	do.	2.25
Alstonia scholaris .....	80.13	14.90	3.68	do.	1.15
Erythrina indica .....	81.23	14.02	3.50	do.	1.10
Sonneratia acida .....	76.85	16.80	3.90	do.	2.40

TABLE No. 3.

Mixture of 0.645 gm. of KNO <sub>3</sub> and 0.130 gm. of charcoal made from: Combustion.	Duration of resi- due in gramme.	Weight
Pithecolobium dulce ... 16 secs.	0.388	
Sesbania grandiflora .... 15 do.	0.378	
Hibiscus tiliaceus .....	0.395	
Alstonia scholaris .....	0.362	
Erythrina indica .....	0.375	
Sonneratia acida .....	0.450	

### BOARD OF EDUCATION.

ARRANGEMENTS AND CONDITIONS FOR THE  
AWARD OF NATIONAL CERTIFICATES IN  
CHEMISTRY TO STUDENTS IN TECHNICAL  
SCHOOLS AND COLLEGES IN ENGLAND  
AND WALES.

*NOTE.—The Institute of Chemistry is undertaking the functions assigned to it in these Rules at the invitation of the Board of Education. In these Rules the Institute of Chemistry is referred to as the "Institute," and the Board of Education as the "Board."*

1.—The Institute in conjunction with the Board is prepared to approve schemes, submitted by technical schools or colleges, for the award of certificates relating to part-time and full-time grouped courses in chemistry conducted under approved conditions. To avoid possible misunderstanding, the certificates will bear a statement indicating that they are distinct from the Associateship and Fellowship Diplomas awarded by the Institute.

#### PART-TIME COURSES.

2.—Courses for the purpose of a part-time course certificate under these Rules must be carried on for at least 180 hours in each year. If the instruction is given ex-

clusively in evening classes, the course should, as a rule, be carried on for three evenings a week during the school session. These courses are classified as follows:—

(i) *Senior*, adapted to the needs of students who have completed satisfactorily a junior part-time course of two years' duration, or have had full-time continuous education up to the age of 15 or 16. Senior courses must extend over at least three years; and should include, in addition to Chemistry, suitable Physics and Mathematics as cognate subjects. Certificates relating to senior courses will be termed "Part-time Course Certificates in Chemistry (Ordinary)."

(ii) *Advanced*, adapted to the needs of students who have completed satisfactorily a senior part-time course or are otherwise suitably qualified (see paragraph 5), and aim at reaching, within the limits of the subjects covered by them, the standard of university work. Advanced courses must extend over at least two years; and should include, in addition to Chemistry, suitable cognate subjects. They may include the study of the application to chemical practice of scientific principles with which the students have become familiar.\* Certificates relating to advanced courses will be termed "Part-time Course Certificates in Chemistry (Higher)."

As a rule, the whole of a part-time course must be taken by the student at one school, but subject to previous approval by the Institute and the Board different years

\* With the approval of the Institute and the Board this study may, in certain subjects, be commenced in the third year of a senior course.

of the course may be assigned to different schools with suitably co-ordinated curricula; and the courses of instruction previously taken by a student who has migrated from one area to another, or by a student who has received satisfactory instruction in science at a secondary school or elsewhere, may be accepted in lieu of such portion of a part-time course, other than the final year, as may be approved previously by the Institute and the Board in each case.

The Part-time Course Certificates (Ordinary and Higher) will record the subjects constituting the course.

#### FULL-TIME COURSES.

3.—Courses for the purpose of a full-time course certificate under these Rules are classified as follows:—

(i) *Full-time Course in Chemistry*, suitable for students who have attended a secondary school up to the age of 16. Full-time courses in Chemistry must extend over at least three years, and should include, in addition to Chemistry, suitable Physics, Mathematics, and one or more modern languages, and may include other cognate subjects. Certificates relating to full-time courses in Chemistry will be termed "Full-time Course Certificates in Chemistry."

(ii) *Full-time Course in Applied Chemistry*, restricted to students who have completed satisfactorily a full-time course in Chemistry, or an advanced part-time course in Chemistry, or other course approved by the Institute and the Board. Full-time courses in Applied Chemistry must extend over at least one year; and should include, in addition to Chemistry, suitable cognate subjects, one of which involves the study of the application to chemical practice of scientific principles with which the students have become familiar. Certificates relating to full-time courses in Applied Chemistry will be termed "Full-time Course Certificates in Applied Chemistry."

As a rule, the whole of a full-time course must be taken by the student at one school, but the Institute and the Board may approve, exceptionally, arrangements for assigning portions of the course to different schools.

The Full-time Course Certificates in Chemistry and in Applied Chemistry will record the subjects constituting the course.

#### APPROVAL OF SCHEMES.

4.—Schemes for the joint approval of the

Institute and the Board must be submitted in accordance with the instructions of paragraph 13. Before approving a scheme, the Institute and the Board will require to be satisfied, for the purposes of the courses under these Rules, as to the equipment of the school, the qualifications of the staff, and the curriculum and syllabuses of instruction in the several subjects.

The approval of a school in respect of equipment, staffing, etc., for the purposes of the courses under these Rules will not necessarily imply that the school may be recognised under the Institute's Regulations as suitable for the training of candidates for the examinations for the Associateship and Fellowship of the Institute; nor will recognition of a school for grant under the Board's Regulations for Technical Schools, etc., necessarily imply that the conditions in regard to equipment, staffing, etc., are such as the Institute and the Board can accept for the purposes of the award of national certificates.

5.—Steps must be taken to secure that students are not admitted to the courses unless they are qualified to profit by them. For the present, evidence of having passed an approved preliminary examination prior to admission to a senior part-time course will not be required. For students in an advanced part-time course who have not completed a senior part-time course, evidence satisfactory to the Institute and the Board as to the attainment of the standard of the Part-time Course Certificate (Ordinary) must be produced. Normally, evidence of having passed an approved preliminary examination prior to admission to a full-time course will be required, except for students who have completed an advanced part-time course.

6.—The conditions of a scheme with respect to home work, laboratory work and records, and examinations (see paragraph 7) prior to the final year of the course, must be submitted for the approval of the Institute and the Board.

7.—Examinations, including practical tests in appropriate subjects, upon the courses of study detailed in the syllabuses constituting part of the approved scheme must be held in each year of the course. These examinations must be held by the teachers, or by an examining body duly approved for the purpose by the Institute and the Board; and for the examination in the final year of the course the examiners must be associated with assessors appointed by the Institute (see paragraph 9).

When a common examination is held in connection with the award both of national certificates and of school or college certificates or diplomas, it will be a condition of approval of a scheme that no candidate shall be awarded a school or college certificate or diploma on the result of such examination in any year in which he has failed to obtain a national certificate.

#### EXAMINATIONS.

8.—A memorandum prepared by the Institute and the Board as to the conduct and supervision of the final examinations under these Rules can be obtained from the Board, and arrangements in conformity therewith must be made by the school or college authorities. The examinations will be open to inspection by His Majesty's Inspectors.

The final practical examinations should be conducted, so far as possible, under such conditions as to time allowance and library facilities as would obtain in ordinary chemical practice.

9.—To satisfy the Institute and the Board in respect both of the standard of the questions set and of the marking of the examination scripts, the Institute will appoint assessors who will act under the joint control of the Institute and the Board.

The assessors will revise the examination papers set at the end of the final year of the course, and will have the option of substituting questions up to 40 per cent. of the total number of questions set. They may make any questions compulsory, provided that the number so made compulsory shall not exceed about 40 per cent. of the number to be answered.

The marking by the examiners of the scripts worked in the final examination will be subject to revision by the assessors, and the marks as accepted or revised by them will be taken into account as explained below for the purpose of awarding certificates, and, in respect of advanced part-time courses and of full-time courses, for the purpose of awarding distinctions in accordance with the conditions of paragraph 11. The assessors may also satisfy themselves with regard to the amount and standard of the laboratory work done by each student throughout the course, as recorded in the laboratory notebooks (see paragraph 19).

#### CONDITIONS OF AWARD OF CERTIFICATES.

10.—To qualify for the award of a certificate a candidate must have:—

(i) made not less than 60 per cent. of

the possible attendances in each year of the course;

(ii) fulfilled the conditions of the approved scheme with respect to examinations, home work, and laboratory work and records in each year of the course prior to the final year;\*

(iii) obtained not less than 40 per cent. of the possible marks in each subject in the final examination;

(iv) obtained in the final year not less than 40 per cent. of the possible marks for home work and for laboratory work and records respectively in each subject for which such marks are to be awarded under the approved scheme;

(v) obtained in the final year not less than 50 per cent. of the grand total of possible marks. The possible marks in the final theoretical examination should constitute 40 per cent., and in the final practical examination 30 per cent. of this grand total; the remaining 30 per cent. should be the possible marks for home work and for laboratory work and records for the final year.

The Institute and the Board may require the submission of the school or college records of attendance, the testimonies of studies, the laboratory notebooks, and the worked papers of any candidate to whom the issue of a certificate is desired.

11.—Distinction may be awarded to any candidate qualified to receive a Part-time Course Certificate in Chemistry (Higher), or a Full-time Course Certificate in Chemistry, or a Full-time Course Certificate in Applied Chemistry, who gains not less than 80 per cent. of the possible marks in the final examination in any subject of the final year of the course. Subject to the previous approval of the Institute and the Board, a candidate may take in such final examination any branch of chemistry or of applied chemistry studied in an earlier year of the course, but not in the final year, and may be awarded distinction in any branch so taken, provided the conditions of this paragraph have been fulfilled. The certificate will record any award of distinction.

12.—For the present the Institute and the Board may decide to issue certificates in

\* A candidate failing to obtain the approved minimum percentage marks for home work, or for laboratory work and records, or for examinations, in any class of a year prior to the final year of the course must be required to attend such class again.

respect of a course taken by students who have not fulfilled completely the prescribed conditions, subject to the fulfilment of such conditions in regard to the last year of the course.

#### SUBMISSION OF SCHEMES.

13.—Applications for the joint approval of the Institute and the Board of new and revised schemes must be submitted by the correspondent of the school or college in the first instance to the Board, from whom the necessary forms of application and all other forms required under these Rules may be obtained. Applications in respect of part-time courses should be made on Form 285 T. in duplicate, and those in respect of full-time courses on Form 286 T. in triplicate, not later than 30th September in the school year for which approval is desired. In subsequent years, unless alterations of an approved scheme are proposed by the school or college, or are required by the Institute and the Board, a renewed application for approval need not be submitted.

#### DUTIES OF EXAMINATIONS OFFICERS.

14.—Each school or college must appoint an examinations officer to conduct on behalf of the school or college the necessary correspondence with the Institute or with the Board in connection with the examinations. The name and address of this officer must be notified to the Institute and to the Board.

15.—The examinations officer must advise the Institute on Form 287 T., not later than 31st January in the final year of each course, of the probable number of candidates expected to take the final examination in that year.

16.—Not less than two months before the date of the commencement of the examinations, the examinations officer must submit to the Institute for transmission to the assessors, draft examination papers for the examinations in the final years of the courses, and syllabuses of the work which will be completed during the year.

17.—At least one month before the date of the commencement of the examinations, the examinations officer must inform the Institute on Form 288 T. of the number of candidates entered for the examinations to be held in the final years of the courses, and must forward the fees to the Institute (see paragraphs 21 and 22).

18.—The examinations officer will be responsible for the conduct and supervision of

the final examinations in conformity with these Rules and with the memorandum mentioned in paragraph 8, and for the safe custody of the examination papers as revised by the assessors and of the worked examination scripts.

As soon as possible after the scripts of the examination of the final year have been marked by the examiners, the examinations officer must forward them to the Institute, together with schedules of marks on Forms 289 T. and 290 T.

These schedules of marks will exhibit the records of the candidates for the several years of their courses in respect of

- (i) attendance;
- (ii) marks for home work, and for laboratory work and records;
- (iii) examination marks.

The number of marks awarded in connection with each paper set, or in respect of home work and of laboratory work and records, will be stated on the schedules in each instance as a percentage of the maximum marks severally obtainable. Provision will be made on the schedule forms for any recommendations or remarks the teachers may wish to make.

19.—If required, the examinations officer must transmit immediately to the Institute, at any time within three months from the last day of the final examination, any candidate's laboratory notebooks for each year of the course, such notebooks to be attested duly by the teacher of each subject. During the same period he must be prepared to produce for the information of His Majesty's Inspector any such laboratory notebooks not in the custody of the Institute. In due course, any notebooks requisitioned by the Institute will be returned to the examinations officer.

20.—The Institute will issue to the examinations officer a list of the results showing the names of the successful candidates and any awards of distinction; and as soon as possible thereafter the certificates will be sent to the examinations officer. The school or college authorities must keep a register containing the names of the students of the school or college to whom certificates have been awarded. The Institute and the Board will keep registers of all certificates awarded by them under these Rules.

#### FEEES AND CORRESPONDENCE WITH THE INSTITUTE.

21.—For the present the following scale of fees has been adopted:—

(i) *Part-time Course Certificate*.—Fee to be paid by the school or college authorities in respect of each group of candidates entered for a final examination of a senior or advanced course: Guineas.

Senior: In respect of the first group	5
In respect of each additional group	2½
Advanced: In respect of the first group	5
In respect of each additional group	2½
Fee to be paid in respect of each candidate entering for a final examination	7/6

(ii) *Full-time Course Certificate*.—Fee to be paid by the school or college authorities in respect of each group of candidates entered for a final examination in Chemistry or Applied Chemistry: Guineas.

Chemistry: In respect of the first group	10
In respect of each additional group	5
Applied Chemistry: In respect of the first group	10
In respect of each additional group	5
Fee to be paid in respect of each candidate entering for a final examination	15/-

22.—All cheques or postal orders should be made payable to The Institute of Chemistry and crossed Westminster Bank, Ltd.; and all correspondence with the Institute in connection with any matters arising out of these Rules should be prepaid, and should be addressed to—

The Registrar,  
The Institute of Chemistry,  
30, Russell Square,  
London, W.C.1.

#### BOARD OF TRADE ANNOUNCEMENT. DYESTUFFS ADVISORY LICENSING COMMITTEE.

##### *Applications for Licences in July.*

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during July, has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee.

The total number of applications received during the month was 371, of which 264 were from merchants and dealers. To these should be added the 24 cases outstanding on the 1st July, making a total for the month of 395. These were dealt with as follows:—

Granted—246 (of which 227 were dealt with within 7 days of receipt).

Referred to British makers of similar products—70 (of which 66 were dealt with within 7 days of receipt).

Referred to Reparation supplies available—50 (all dealt with within 2 days of receipt).

Outstanding on the 31st July—29.

Of the total of 395 applications received, 336, or 85 per cent., were dealt with within 4 days of receipt.

Board of Trade,  
8th August, 1923.

#### LOWEST TEMPERATURE YET OBTAINED.

The lecture by Professor Dr. H. Kamerlingh Onnes on the *Lowest Temperature yet Obtained*, which is given in the Transactions of the Faraday Society for December, 1922, deals with a subject of very great interest. As soon as the efforts to liquefy helium had succeeded, it was of course investigated whether it could be solidified also. This was even tried on the same day on which helium had for the first time been seen as a liquid. The method used was that of evaporation under reduced pressure.

After describing the apparatus and preliminary experiments, Professor Onnes gives the following account of the crucial experiment.

“Early in the morning the preparation of 24 litres of liquid hydrogen was commenced, the previous day having been spent, on the one hand, in evacuating the apparatus and further putting it in working order, and, on the other hand, in preparing a sufficient quantity (more than 50 litres) of liquid air. Meanwhile, the following preparations were carried out: the helium circulation was further put in order; the pump, which had to remove the hydrogen from the helium liquefier at reduced pressure, was started; the space reserved for the liquid air used in cooling the hydrogen was next filled, and the liquid hydrogen space filled, after having been first cooled with dry cold hydrogen gas. At 12 o'clock the liquid helium could be syphoned over into the cryostat, after which we proceeded to cool this bath further by evaporation and refilling by means of the helium circulation. At 1 o'clock the condensation of the helium into the evaporation apparatus could be commenced, and the bottom part of the



evaporation glass was filled up to somewhat above the double-walled cap mentioned earlier. At about 3 o'clock this helium had evaporated so far as to occupy only the lower part of the evaporation flask, the evaporation taking place first under the action of the auxiliary pump complex, later on under that of the combined high-vacuum and auxiliary pumps, which serve for the removal of the helium from the evaporation apparatus. The evaporation was further observed alternately with the naked eye and with the telescope of a cathetometer, the screens around the evaporation flask being kept shut as long as possible. Neither by means of the stirrer nor with the naked eye or with the telescope could anything be observed that pointed to the solidification of the helium, even at the lowest vapour pressure observed; the liquid retained its great mobility throughout."

Professor Onnes sums up this part of the research as follows: "Returning to the question of the solidification of helium, we come to the following conclusion: as there is provisionally no doubt that helium has a maximum density, and as it is even not solidified at a temperature below the half of that of the maximum density, we cannot escape the question whether helium will not remain perhaps liquid, even if it is cooled to the absolute zero."

The result of the experiments recorded by Professor Onnes was the attainment of a temperature of 0.82 K., which he sums up as follows: "Taking into account the uncertainty of the extrapolation, it will be better to say that the lowest temperature yet attained is some hundredths of a degree below 0.9° K."

"If it is considered that our knowledge of atomic structure renders improbable that another substance could be discovered or obtained in another way, more volatile than helium, then the limit indicated would seem an absolute one set to us in the obtaining of yet lower temperatures.

We cannot accept such a limit otherwise than as a provisional one. There are even now definite problems which require to be treated in the domain beyond the seemingly impenetrable barrier. A simple example is the question whether a metal such as gold can be made super-conductive by cooling it more than we have been able to do. This kind of problem reminds us of the problem of the liquefying of the permanent gases. They withstood the efforts of the great experimenter whose glorious name it attached

to your Society. Half a century later, the liquefaction of hydrogen, the most incoercible gas with which Faraday had operated, was the brilliant achievement of the latest of his successors in office at the Royal Institution: Sir James Dewar. We may feel sure that the difficulty which has now arisen in our way will be overcome also, and that the first thing needed is long and patient investigation of the properties of matter at the lowest temperature we can reach."

"The Vacuum-Spark Spectrum of Silicon," by R. A. Sawyer and R. F. Paton.—(*Astrophysical Journal*, June, 1923.)

The most recent work on the spectrum of silicon was done by Sir William Crookes in 1914. He succeeded in obtaining some rather pure samples of silicon, and using a condensed spark between electrodes of this silicon, photographed the spectrum with a prism spectrograph. The rapid oxidation of the silicon made it very difficult to maintain the spark, and necessitated long exposures. His work covered the region  $\lambda$  6500 to  $\lambda$  2100, and he published the wavelengths of 48 lines, including most of the lines previously recorded. This investigation was the most thorough work that had been done on silicon up to that time. Since the work of Crookes, Fowler has mentioned observing four lines in the visible region of the spectrum, not previously observed; and McLennan has extended the investigation into the extreme ultra-violet, cataloguing some seventeen additional lines.

A comparison of the results of all the work that has been done on silicon brings out the fact that no two observers have the same list of lines, and also shows that, even in the lines that have been recorded by several observers, the disagreement in wave-length seems almost unaccountably large. This disagreement may be partly accounted for, however, by the fact that many of the silicon lines are especially broad and hazy when produced at atmospheric pressure.

With the discovery of the vacuum-spark, a new source of light became available that seemed to have particular advantages in this problem. The use of the vacuum-spark in extending the spectrum into the extreme ultra-violet, had given results which led to the expectation that it might give new information in the rest of the spectrum. With this in mind, it was decided to photograph the vacuum-spark of silicon in

the region covered by Crookes, hoping that the results might give more accurate information concerning the wave-lengths of some of the lines, and even add to the already known list. In adapting the vacuum-spark to silicon, it was found necessary to use high voltage and extremely good vacua; but once obtained, the spark was brilliant, of a reddish yellow colour, and resembled the vacuum-spark of carbon.

A description of the apparatus used and tables of the observed lines are then given, of which the following is the author's abstract:—

*Vacuum-spark spectrum of silicon*  $\lambda$  6700— $\lambda$  2100. Silicon electrodes less than a millimeter apart were mounted in a suitably designed brass box with a quartz window, the best obtainable vacuum was produced, and a highly condensed spark was obtained by the use of 70,000 volts. Lines of iron, aluminum, calcium and oxygen and the strongest lines of hydrogen, nitrogen, copper, zinc and titanium appeared as impurities. The wave-lengths of 227 lines attributed to silicon in the region  $\lambda$  6700— $\lambda$  2100, together with the measurements of other observers, are given in Table 1. An additional 75 lines, listed in Table 2, are given as doubtful, since they were faint lines appearing on only one plate. In the intervals,  $\lambda$  6700— $\lambda$  5500 and  $\lambda$  4070— $\lambda$  5500— $\lambda$  4070 and  $\lambda$  3400— $\lambda$  2100 to  $\lambda$  3400, the wave-lengths are believed to be accurate to within 0.2A, and in the intervals within 0.1A.

#### X-RAY PROTECTIVE MATERIALS.

By G. W. C. KAYE, O.B.E., M.A., D.Sc.,  
AND E. A. OWEN, M.A., D.Sc., THE  
NATIONAL PHYSICAL LABORATORY.

(From a Paper read at a Joint Meeting of  
the Physical Society of London and  
Röntgen Society.)

The steady addition to the already lengthy list of casualties to hospital and other X-ray workers led to the formation nearly two years ago of an X-ray and Radium Protection Committee (under the chairmanship of Sir Humphry Rolleston), which drew up a series of recommendations for the better protection and general improvement of the working conditions of the X-ray operator. These recommendations

have resulted in a large number of X-ray protective materials being submitted for test to the National Physical Laboratory, which from the outset agreed to work in co-operation with the Committee, and has inspected the X-ray departments of many hospitals from the point of view of the Committee's recommendations.

It is well known that the absorption of an atom is greatest for those X-rays which have wave-lengths slightly shorter than one or other of its characteristic radiations, and partly with this in mind it was thought that it would be of value to ascertain the protective efficiencies of the various materials which are commercially available for the purpose of affording protection to the radiologist. Among these are sheet lead, lead impregnated rubber, lead glass, and various wall compositions such as barium-sulphate plasters, &c. The choice of one or other is normally dictated by considerations such as dielectric strength, portability, electrical and thermal conductivity, and not least by price.

Protection may be afforded in a variety of ways in practice. For example, by mounting the tube in a surrounding tube box suitably designed to permit the freedom of movement desired, or where this is impracticable the operator and his controls are situated behind a screen or wall which is constructed to give the necessary protection. Less frequently and conveniently the operator is "armoured" and wears protective aprons, gloves, face mask or goggles.

To the inexperienced the practice of speaking of percentage absorption may be misleading and calculated to give a wrong impression of the value of a protective material. It is not always realised how rapid the rate of absorption is with thin layers, and how slow with thicker layers. For example, in the case of tungsten X-rays generated at 120,000 volts, a sheet of lead only 0.1 mm. thick absorbs as much as 80 per cent. of the radiation, whereas a sheet 2 mm. thick only increases this figure to 99.4 per cent.

For simplicity, therefore, the Protection Committee recommended that the protection afforded by a material should always be referred to in terms of the equivalent thickness of lead. This use of lead as a standard of reference, while not wholly free from objection, is very convenient for the approximate accuracy which suffices in practice, especially in dealing with composite or laminated materials as the lead values of

the several layers can be regarded as additive. The Committee laid down certain thicknesses of lead which it regarded as the minima which should be employed under specified conditions; and, in view of the

very unsatisfactory conditions which prevail in the majority of X-ray installations in this country, we have been led to put on record some of our measurements in this connection.

Material.	Density.	Lead Equivalent.
Lead Rubber—(60 different samples) .....	3.7 to 6.5	0.25 to 0.45
Lead Glass—(40 different samples) ... ..	3.2 to 4.1	0.12 to 0.20
Metals—		
Aluminium .....	2.7	0.011
Brass .....	8.4	0.25
Steel .....	7.8	0.15
Miscellaneous—		
Water .....	1	0.004
50 per cent. red lead, 50 per cent. litharge	—	0.3
Ordinary rubber .....	1.2 to 1.7	0.02 to 0.05
Concrete—		
4 stone chippings, 2 washed sand, 1 cement .....	2.1	0.012
4 clinker, 1 cement .....	1.5	0.010
4 granite, 1 cement .....	2.1	0.013
Roman mortar .....	1.5	0.009
20 chalk, 1 cement .....	1.6	0.011
6 sand, 1 lime .....	1.8	0.009
Coke breeze .....	1.0	0.004
Bricks—		
Fletton brick (red) .....	1.6	0.010
Stock brick (yellow) .....	1.4	0.008
Diatomaceous brick .....	0.6	0.003
Protective Wall Plasters—		
(1) 55 p.c. Native Ba Co <sub>3</sub> , 45 p.c. Ca So <sub>4</sub>	2.0	0.001
(2) 33 p.c. Ba So <sub>4</sub> , 33 p.c. sand, 33 p.c. cement .....	1.5	0.048
(3) 33 p.c. coarse Ba So <sub>4</sub> , 33 p.c. fine Ba So <sub>4</sub> , 33 p.c. cement*	2.3	0.12
Woods—		
Ash .....	0.73	0.0013
Balsa .....	0.096	0.0001
Bass .....	0.48	0.0005
Fir .....	0.52	0.0008
Mahogany .....	0.49 to 0.68	0.0006 to 0.0011
Oak .....	0.65	0.0008
White Pine .....	0.47	0.0006
Pitch Pine .....	0.53 to 0.56	0.0008
Spruce .....	0.41 to 0.43	0.0004 to 0.0006
Teak .....	0.58 to 0.76	0.0006 to 0.0011
Walnut .....	0.64	0.0008

\* Mixture suggested by Mr. P. J. Neate.

Incidentally, sheet lead is commercially described and sold by its weight per superficial foot, "2lb. lead" referring to sheet lead weighing 2lb. per sq. foot. In this connection the following table may be useful:

Weight.	Thickness.
2 lb. lead .....	0.8 mm.
3   "   .....	1.25   "
4   "   .....	1.7   "
5   "   .....	2.15   "
6   "   .....	2.6   "
7   "   .....	3.05   "
8   "   .....	3.5   "
9   "   .....	3.95   "
10   "   .....	4.3   "
11   "   .....	4.75   "
12   "   .....	5.2   "

There is some tendency at the present time to employ baryta and other plasters in lieu of lead. We give the lead equivalents of three of these plasters. It may be remarked, to take the case of mixture No. 2, that 60 mm. (nearly 2½ inches) thickness will be required to give the protection of 3 mm. of lead, and that the weight of the plaster is nearly three times that of the lead. These figures would be more favourable for plaster No. 3. We have no knowledge of the costs of these plasters as compared with lead, nor of the cost of the labour involved in erection.

Certain plasters have been devised containing iron turnings. They possess no special merit as regards absorption, and the tendency to rust is a disadvantage.

#### TUBE BOXES.

Protective tube boxes, if constructed of lead, have to be of dimensions sufficiently generous to prevent sparking between the bulb and the box. If, however, the tube box is required to be in close proximity to the bulb, the former commonly takes the form of a lead glass bowl, or, alternatively, a wooden box with several layers of lead-rubber lining or wrapping. The open glass bowl is open to grave criticism: it is constructed of lead glass, usually affording, as our measurements show, a total protection of from 0.5 to 0.7 mm. lead; but in many directions, owing to its design, it affords no protection whatever. In our experience, where this type of shield is alone employed, it is often possible to take a radiograph of the hand in any part of a room where a tube is working. The bowl should be pro-

vided with some kind of cover and the material increased in effectiveness.

The type of double hemispherical shield supplied for radiator Coolidge tubes is much better, in that it completely encloses the tube. The different shields (whether tinted blue or yellow) which we have tested, have a lead equivalent of about 0.2, the total protection provided ranging between 1.2 and 1.5 mm. lead. The Protection Committee recommends not less than 2 mm. for exciting voltages below 100,000. We refer again to the question of lead glass in connection with protective windows, etc.

Different makes of lead rubber differ in protective value by 100 per cent., and the importance of this fact should be stressed. Care should be taken that the lead rubber is not cut away locally when the box is being constructed.

The choice of lead rubber or lead glass in preference to lead sheet is usually dictated by the fact that the former are electrical insulators, at any rate to a limited extent. The resistivity of lead rubber is usually of the order of several thousand megohm centimetres. The insulating value may be greatly improved by including a layer of micanite, ordinary rubber, or other suitable insulator among the layers of lead rubber.

Measurements of the dielectric strength have been made in the Electrical Department of the Laboratory on a considerable number of samples. Two circular electrodes 1½ in. in diameter with rounded edges were placed in contact with opposite sides of the material, an alternating potential of approximately sine wave form being applied and steadily increased from zero until the material punctured. For good specimens of lead rubber the breakdown voltage was about 5,000 to 12,000 R.M.S. volts per millimetre thickness. In other cases the values were a good deal less, and on occasion the material acted as a conductor. For lead glass the values ranged from about 5,000 to 9,000 R.M.S. volts per millimetre.

One other point may be referred to. In a prolonged run, especially with a Coolidge tube, a great deal of heat has to be got rid of, and it is usually advisable to provide for ventilation of the tube box; in that event the openings should be properly safeguarded from a protection standpoint. A knowledge of the thermal conductivity of the several protective materials may be useful in this connection. Measurements at the Laboratory show that the values of the thermal

conductivity at room temperature are as follows in c.g.s. Centigrade units:—

Woods (various)	About	0.0003
Ordinary rubber	„	0.0008 to 0.0011*
Lead rubber	.... „	0.0003 to 0.0007
Lead glass	..... „	0.002
Lead	..... „	0.08

\* Depending on the mineral content.

If considerations of weight are of first importance, then lead sheet is almost always the lightest among the protective materials commonly employed for tube boxes. For example, the protective values of lead rubber range between about 0.25 and 0.55, and the densities between about 3.7 and 6.5. On the average, lead rubber is about 10 per cent heavier than sheet lead, affording the same protection, though it may be as much as 25 per cent. and as little as 5 per cent.

Similarly with lead glass the protective values commonly lie between 0.12 and 0.20, and the densities between 3.2 and 4.1. On the average, lead glass is about twice as heavy as sheet lead, affording the same protection, the figures ranging from about 1.75 to 2.5.

These results (as with those for the screen materials) are, of course, predictable, as it is known that a heavy atom is ordinarily much more absorbent than a light. For the same reason, in the case of two composite materials, each containing a mixture of atoms and having the same density, the one containing a higher proportion of heavy atoms will usually have a higher absorption factor. With lead rubber the lack of proportionality between density and lead value is sometimes pronounced, and of two samples the one with the lower density may have the higher lead equivalent.

Diaphragms of the iris type are often fitted to tube boxes. The leaves are usually much too transparent. They should provide protection equal to not less than 3 mm. of lead, and the simpler rectangular diaphragm with two motions is a more practical job.

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### IRON AND STEEL INSTITUTE.

MILAN MEETING, SEPTEMBER 17 & 18, 1923.

In accordance with previous announcements, the Autumn Meeting of the Iron and

Steel Institute will be held at the Chamber of Commerce, Milan (via Mercanti 2-4), on Monday and Tuesday, September 17 and 18, commencing at 9.30 a.m. on each day.

At the conclusion of the meeting visits have been arranged to Florence, Rome, Piombino, Leghorn, Genoa and Turin.

The following is the list of papers which it is expected will be submitted to the meeting:

C. R. AUSTIN, *Alloys in the Ternary System Iron-Chromium-Carbon.*

E. D. CAMPBELL, W. L. FINK, and J. F. ROSS, *The Iron-Iron Carbide Equilibrium in Dry Hydrogen at 950° C.*

E. D. CAMPBELL, J. F. ROSS, and W. L. FINK, *The relative efficiency of Dry and of Moist Hydrogen on the Decarburisation of Steel at 950° C., and the effect of Hydrogen on the Phosphorus Content.*

C. A. EDWARDS and L. B. PFEIL, *A Note on Coarse Corrugation in Mild Steel Sheets.*

G. E. FALCK, *The Iron and Steel Industry of Italy.*

F. GIOLLITI, *The Complex Action of Manganese and of other so-called Deoxidising Agents in the Manufacture of Steel.*

W. T. GRIFFITHS, *The Change Points in some Nickel-Chromium Steels.*

W. H. HATFIELD, *The Influence of Nickel and Chromium upon the Solubility of Steel (in relation to Corrosion).*

CESARE MARTELLI and TITO SOTGIA, *The Iron Ore Mines of Nurra (Sardinia).*

A. PORTEVIN, *The Morphology of Proeutectoid Cementite.*

A. PORTEVIN, *The Corrosion Cracking of Steel under the Influence of Internal Stresses.*

S. H. REES, *The effect of Low Temperature Annealing on some Mechanical Properties of Cold Drawn Steels.*

H. STYRI, *Theory and Practice of Steel Refining.*

C. VANZETTI, *The Manufacture of Heavy Steel Castings from Small Converters.*

H. C. WANG, *Grain Growth in Iron and Steel.*

28, Victoria Street, London, S.W.1.  
August 13, 1923.

#### THE CHEMICAL SOCIETY.

It has been decided to separate the Transactions and the Abstracts, and from January, 1924, these will appear monthly as distinct volumes. A new feature in the Transactions will be the inclusion from time

to time of "Notes" dealing with, for example, improved methods of preparation, modification of standard apparatus, and other matters requiring only brief notice.

#### "THE CHEMIST IN RELATION TO THE SAFEGUARDING OF INDUSTRIES."

This, the last of my headings, has reference to two recent Acts of Parliament, which you will all know something about, namely, the Dye-Stuffs Import Regulations Act of 1920, and the Safeguarding of Industries Act of 1921. The former prohibits the importation into this country of synthetic organic dyestuffs, etc., except under licence from the Board of Trade. Of course, all that is to the good so far as the protection of the home chemist is concerned. I think the Safeguarding of Industries Act also will be found, in the long run, to be for the benefit of the chemist rather than otherwise. That Act imposes a duty of one-third the value of the goods upon certain enumerated articles, among which are found nearly all the mechanical apparatus of the chemist, and, in addition, practically all the raw material which the chemist uses in his researches. At first sight it might be thought a little against the interest of the chemist that he should have to pay more for his raw materials and for his apparatus, by reason of these high import duties, because, I suppose, there are many of these things which, even now, can only be obtained from abroad; but in the long run it must be to the benefit of the chemist and the Empire that the production of all these things at home should be promoted. When the crisis came in 1914 we had not got, and had not the facilities for producing, many essential substances and apparatus. If we can make these things at home, then not only will there be increased employment of chemists, but when we come to another crisis we shall be better provided in that respect than we were then. I think the provisions of this Act will help to bring that about.—(From the Lecture recently delivered before the Institute of Chemistry, by Evan James MacGillwray.)

#### A SENSITIVE ELECTROSCOPE.

By TAKEO SHIMIZU.

(*Jap. J. Phys.*, I. (1922), 107-111, with 2 fig.)

The electroscopie described in this paper

is a modification of that of Mr. C. T. R. Wilson. It consists of a fine silvered glass fibre suspended freely at the centre and four metallic plates, two large and two small, placed symmetrically on both sides of it. The larger ones are about as long as the fibre and stand vertically facing each other on each side. The smaller ones stand also vertically but below the locus of the lower end of the fibre at some distance from each other and situated between the fibre and the respective larger plates. The two plates on either side form a single electric system and the two systems are kept at the same potential, while the fibre is charged to a high auxiliary voltage. When the electroscopie is to be used, one of the systems is isolated and connected to the object. The two inner smaller plates play the part of a stabilizer and a comparatively high sensibility can be obtained in virtue of their presence. In favourable cases a sensibility of about 5,000 scale divisions per volt was obtained, although such a sensibility may not be suited to the deflection method, owing to various difficulties. But as the instrument keeps a very constant zero position by its design, it may be employed as a sensitive zero indicator.

#### ON THE STRUCTURE OF THE SECOND CYANOGEN BAND.

By JUNZO OKUBO.

(*Sci. Dep. Tôhoku Imp. Univ.*, Ser. I., XI. (1922), 55-86, with 1 pl.)

The second cyanogen band having the first head at  $\lambda$  4216 Å emitted by the ordinary carbon arc in air was examined. The instrument used in this experiment was a concave grating of a radius of curvature 6.55 m. with 5,910 lines per cm. and 77,273 lines in all. Acheson regraphitized carbon rods were used. The wave lengths of 1,555 lines lying between  $\lambda$  4216 and 3900 Å were accurately determined in the international unit. The second band contains many doublets, some of which have been described as singlets by many previous investigators. Three remarkable series were traced, and their intensity distributions described. The wave lengths of the heads of four bands produced by cyanogen were measured, and it is shown that there exist some simple relations among the wave numbers of consecutive heads.

## ON THE BAND SPECTRUM ASSOCIATED WITH HELIUM.

BY YUTAKA TAKAHASHI.

*(Proc. Phys.-Math. Soc. Japan, Ser. III., IV. (1922), 187-194).*

In order to explain the origin of Fowler's series of double headed bands of helium, the author assumes that when a discharge is passing through a helium tube there are produced some short living, unstable molecules, each consisting of two positive nuclei, which are liable to vibrate along the line joining them and to rotate as a whole about the middle point of the line, and electrons, one of which is removed from its stable orbit to another of a higher quantum number. By applying the quantum theory to this model, it is shown that the frequency  $\nu$  of the radiation is of the form:

$$\nu = A(m_1, n_1, m'_1, n'_1) - A(m_2, n_2, m'_2, n'_2),$$

where  $m$  and  $n$  are the radial and azimuthal quantum numbers respectively due to the electron, and  $m'$  and  $n'$  are respectively those due to the nuclei. Different values of  $n'$  correspond to the individual lines of each band, and different values of  $m'$  give rise to the series of the bands, which actually appear as double headed bands as  $m'$  is limited to zero and 1 owing to the instability of the molecule. Two different combinations of  $m$  and  $n$  such as

$$m_1 = 1 + s, n_1 = 2, m_2 = 1, n_2 = 1, s = 0, 1, 2, \dots$$

and

$$m_1 = s, n_1 = 3, m_2 = 0, n_2 = 2, s = 0, 1, 2, \dots$$

are responsible for the two series of the double headed bands detected by Fowler.

## ON THE LANTHANUM VIOLET BANDS AND THE ASSOCIATED LINES.

BY JUNZO OKUBO.

*(Sci. Rep. Tôhoku Imp. Univ., Ser. I., XI. (1922), 95-104, with 1 fig.)*

The structures of the band spectrum emitted from lanthanum nitrate put into a carbon arc were studied with a large concave grating. The wave lengths of the edges of the bands, some of which had been missed by previous investigators, were determined in the new international unit, and the opinion was confirmed that each band is of double structure. In the light of the quantum theory, the bands may be explained as due to molecular rotations caused by line emissions.

## BRITISH STANDARDISED STEEL SAMPLES ISSUED JOINTLY BY THE IRON AND STEEL INSTITUTE AND THE NATIONAL PHYSICAL LABORATORY.

The Standards at present available are:

No. 1.—Sulphur (S.=0.027 p.c.).

No. 2.—Sulphur (S.=0.071 p.c.).

No. 3.—Phosphorus (P.=0.029 p.c.).

No. 5.—Carbon (C.=0.65 p.c.) Acid O—H Steel.

No. 6.—Carbon (C.=0.10 p.c.) Basic O—H Steel.

These Samples are supplied, post free, at 21s. per bottle containing 50 grammes, together with certificate of Standardisation. They can be obtained, by sending order with remittance, direct from:—

The National Physical Laboratory,  
(Metallurgy Dept.), Teddington,  
Middlesex;

or by post or personal application from:—

Dr. C. H. Desch, Dept. of Applied Science, The University, Sheffield.

Dr. C. A. Edwards, The University College, Swansea.

Col. E. L. Johnson, Cleveland Technical Institute, Middlesbrough.

Mr. D. A. MacCallum, West of Scotland Iron & Steel Institute, 93, Hope Street, Glasgow.

Other Samples are in preparation and will be issued when ready.

These samples can also be obtained from all Chemists dealing regularly in laboratory ware.

## NOTICES OF BOOKS.

The July number of the *Bulletin of the Bureau of Bio-technology* contains the following papers:—

*The Occurrence and Effects of Wood-destroying Fungi in Coal Mines.*

*The Examination of Bacteria in Beer Deposits.*

*Water Softening for Spraying Purposes.*

*The Suppression of Insect Pests and Fungoid Diseases.*

The number also contains an Index for Vol. 1. A copy of this Index may be had on application to Messrs. Murphy & Son, Ltd., Cedars Laboratories, Sheen Lane, Mortlake, London, S.W.14.

*The Paper-makers' Directory of all Nations*, published by Dean & Sons, Ltd.,

27, King Street, Covent Garden, price 21s., will be found of value to those interested in paper and the allied trades.

The subject matter is arranged in alphabetical order for easy reference, and contains a large number of trade headings and a classified index to commercial prospectuses.

The work has been produced with the usual thoroughness and care, and cannot fail to be of interest and value in the paper trade.

*Practical Bacteriology for Chemical Students*, by DAVID ELLIS. Longmans, Green & Co., 39, Paternoster Row. Price 4s. 6d. net.

This valuable little book consists chiefly of exercises which are followed in the author's classes in the University of Glasgow, and in the preface it is pointed out that there are many avenues in chemical research that are closed to the investigator owing to lack of knowledge of the elementary principles of bacteriology. The object of the book is to give to the trained chemist sufficient guidance to enable him to master the general principles of the subject. The exercises are so arranged that they can easily be followed by any who desire a grounding in the general principles of bacteriology.

The book opens with a chapter devoted to descriptions of the apparatus used in bacteriological research, and it is very thoroughly illustrated with both drawings and diagrams. In chapter 2 the exercises commence with the preparation of nutrient gelatine and agar-agar. Chapters are given on the staining of bacteria, identification and staining of spores, isolation of bacteria from soils, examination of drinking water and sewage, and many details connected with practical bacteriology.

The work is written in simple language, and is easy to follow. It is quite evident that the author is not only a thorough master of the subject, but also possesses the great qualification of lucid explanation. The book is well indexed, and contains a table of contents. It will be found of very great value to all interested in the subject of which it treats.

#### BOOKS RECEIVED.

*Physikalische Chemie: I., Chemische Reine Stoffe; II., Lösungen*; von DR. ALFRED BENFATH, A. O. Professor der Chemie

an der Universtat Bonn. Pp. VIII. + 107. 1923. Verlag von Theodor Steinkopff, Dresden and Leipzig.

*Practical Physical Chemistry*, by ALEXANDER FINDLAY, M.A., D.Sc., Professor of Chemistry, University of Aberdeen. Pp. XVI. + 298. 4th Edition, 1923. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 7s. 6s. net.

*Petroleum Technologist's Pocket-Book*, revised by ARTHUR W. EASTLAKE. Pp. 546. 1923. Messrs. Charles Griffin & Co., Ltd., Exeter Street, Strand. 15s. net.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancey Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 19834—Buss Akt-Ges.—Apparatus for production of anhydrous tin chloride. Aug. 2.  
 19592—Constant, G.—Reduction of metal oxides. July 31.  
 19600—Naugatuck Chemical Co.—Preparation of reaction product of acetaldehyde and aniline. July 31.  
 19977—Weizmann, C.—Filtration of solutions, etc. Aug. 3.

#### Specifications Published this Week.

- 200851—Thomas, J., and Scottish Dyes, Ltd.—Method of producing anthraquinone sulphonic acids.  
 200902—Du Pont de Nemours and Co., E. I.—Process of manufacturing cyanides.  
 179951—Heinemann, A.—Process of manufacturing formic aldehyde.  
 189107—Barrett Co.—Manufacture of aromatic aldehydes.  
 190123—Soc. Chimique des Usines du Rhone.—Process of manufacture of the calcium salt of acetyl salicylic acid.

#### Abstract Published this Week.

- 199073—Chlorinated montan wax.—Stinnes, H. (Firm of), Mulheim, Germany.

The chlorination of montan wax, obtained by extraction of lignite with solvents, is effected in the presence of water, organic solvents being absent. The montan wax is first suspended in water or an alkaline solution, such as caustic soda solution or milk of lime, and gaseous chlorine passed in; or a suspension of montan wax in hydrochloric acid is treated with chlorate, for example, by the addition of potassium chlorate in the solid form or in aqueous solution. The reaction may be accelerated by the presence of catalysts, such as ferric chloride. The products are useful for insulation purposes, as a substitute for beeswax, and in the preparation of floor polishes, boot creams, &c.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3307.

M. CAREY LEA, CHEMIST.

1823—1897.

By EDGAR F. SMITH, UNIVERSITY OF PENNSYLVANIA.

A hundred years ago (1823), Matthew Carey Lea was born. His contributions to chemistry brought him honour and distinction among his colleagues throughout the world, so that pause may well be made to let them pass in brief review. Few chemists of his day knew him personally; in fact, students of chemistry in this country would probably not give his name if called upon for a list of American scientific worthies, hence a brief consideration of his achievements will be in order. They will augment our pride in the men who wrought in chemistry before these very modern days when, on all sides, there is heard a demand for research, forgetting that the past in chemistry, even in this country, can present many excellent examples of earnest devotion to the purely scientific aspects of chemistry.

Carey Lea (as he was usually called) was a true researcher. His first study, published in 1841, related to the Southern Coal Field of Pennsylvania. His father had expressed the thought that "the hard or highly carbonised anthracite of the eastern end of the Southern coal field changes to bituminous in the western end by nearly regular gradations." The results obtained by Carey Lea showed "that the bituminous qualities of the coal increase with considerable regularity from Tamaqua (the eastern-most end) to Rattling Run (the western-most extremity)."

Lea did this work when he was but eighteen years old, in the laboratory of Booth, Garrett and Blair, where he had gone to familiarise himself with practical chemistry. He loved scientific pursuits. He never went to school or college. His remarkable training was "through the best private tutors procurable." His intellectual powers were immense. He knew literature, mathematics, languages, and the natural and physical sciences.

After his first venture into experimental chemistry he gave himself to the study of law, and was admitted to the Bar in 1847, at the age of 24. But this profession he abandoned and journeyed to Europe, hoping

to regain his health, which had become precarious. However, his hopes were not realised, and he returned to the old laboratory on Arch Street (Booth, Garrett and Blair) with the view of perfecting himself still further in chemistry.

In his earlier days in the Booth, Garrett and Blair laboratory, he had as fellow student in chemistry his brother, Henry Charles Lea, who later in life was regarded as the first and greatest of modern scientific historians. He was the author of seventeen volumes on Mediaeval History and Law. And this same younger brother, at the age of twelve years, was busily engaged in a study of manganic oxide; the results appearing in May, 1841, in the *American Journal of Science*. The paper is interesting and valuable. Few chemists, at the age of twelve, have ventured forth with such an excellent production. He began:

"The peroxide of manganese ( $Mn_2O_3$ ) has never been investigated, as its existence has, until lately, been questioned by some of the first chemists in Europe, and the tendency of its salts to convert themselves into proto-salts, contributed to render it problematical whether it was not merely the protoxide disguised."

Interrupting this digression, it may be remarked that when Carey Lea finally left the Booth, Garrett and Blair laboratory, it was to enter a private laboratory installed in his home at Chestnut Hill. There nearly all his later experimental work was done. But the notebooks of that work were, upon his death, destroyed in accordance with his own desire. Among these was a list, preserved from boyhood, of the chemicals and apparatus imported by his father for his use.

Lea showed a decided penchant for chemical theory. He was much concerned about the chemical properties of atoms and their numerical relations, undertaking to show "that the number of 44.45 plays an important part in the science of stoichiometry, and that the relations which depend upon it are supported, in some cases at least, in a remarkable manner, by analogies of atomic volume." This relation was found to extend to no less than forty-eight of the elements. The first germs of the periodic law, not, however, clearly enunciated, were in his thoughts. And in 1875 and 1876 he published two ingenious papers on the Colour Relations of Ions, Atoms and Molecules.

As early as 1857 Lea became interested in picric acid, giving a new method for its preparation and also descriptions of many new

salts, including the urea and quinine picrates. He concluded that picric acid was wholly unreliable as a test for potash, and, indeed, a better test for soda.

Shortly after the beginning of the Civil War he advised the United States Government that picric acid would be an explosive of greater power than black powder. Its smokelessness appealed to him as an advantage. The Federal Government, however, failed to appreciate the importance of using an explosive outranging anything in use at the time, and it was not until fifty years after that high explosives on a picric acid basis were adopted.

To separate the ethylamines Lea recommended the use of their picrates: triethylamine picrate being extremely insoluble, diethylamine extremely soluble, and ethylamine intermediate. He gave some consideration to the methyl bases and the preparation of urea—with good and definite results. By the interaction of naphthylamine and sulphuric acid he obtained ionaphthine—a new colouring matter. On dropping a bit of gelatine into a mercuric nitrate solution the latter gradually assumed a deep red colouration—a new and valuable test for gelatine. Lea did not regard as reliable the determination of the melting point of methyl oxalate as a means of ascertaining the purity of methyl alcohol (containing ethyl alcohol). For the detection of prussic acid he suggested the addition of a ferrous salt containing a little uranic nitrate, when a beautiful purple coloured precipitate was formed. A great increase of delicacy in the reaction between starch and iodine was observed by Lea on adding chromic acid to the solution. He also wrote on a new method of determining the relative affinities of certain acids which was based on the amount of base which it can retain in the presence of a strong acid selected as a standard of comparison for all acids. Two new methods were proposed by Lea for the reduction of platinic to platinous chloride—one by the action of potassium sulphite, the other by that of alkali hypophosphites. He also demonstrated that a solution of iodoquinine affords a means of detecting free sulphuric acid, even in traces, in presence of combined sulphuric acid.

In a collection of miscellaneous pamphlets, once the property of Carey Lea, are several contributions of Carl Claus on "Chemie der Platinmetalle," fully annotated in the marginal way, thus revealing that Lea had more than ordinary interest in

this very important group. He studied its members with care, using material furnished by his former teacher, James Curtis Booth. Among the new facts disclosed by him is the use of oxalic acid for the first time in purifying ammonium iridium chloride, and the discovery of a reaction for ruthenium which proved most helpful. If to a solution of sodium hyposulphite there be mixed ammonia and a few drops of ruthenium sesquichloride, a magnificent red-purple liquid will be produced, which, unless quite dilute, will be black by transmitted light. The chief value of this test was found to lie in the fact that it is capable of detecting ruthenium in the presence of iridium. Lea thought it valuable in testing the purity of iridium for "if the suspected iridium salt be boiled with hydrochloric acid, and ammonia added until the liquid assumes a pale olive colour, then, on adding the hyposulphite and boiling, any increase of colour indicates the presence of impurity. If the liquid acquires a red colour, ruthenium is present; if a wine colour, platinum is probably present, and if brown, palladium is indicated." Lea applied ruthenium sesquichloride to detect sodium hyposulphite.

An adequate idea of Lea's voluminous work, as investigator, cannot be given in a narrow compass, such as this article. The student should turn to the pages of the *American Journal of Science*, beginning with the year 1858, and read forward to the year 1897, then some deduction may be drawn of the vastness of Lea's labours. These papers deserve very careful study. There is such an abundance of originality in them. In the volume of *The Chemical News* for 1862 will also be found four additional contributions. A review of all this material would furnish many topics for seminar consideration.

But the greatest of all Lea's efforts to extend the borders of human knowledge are those dealing with the chemistry of light; for in photochemistry he was a true pioneer. He blazed the way. Quite early in his life the startling invention of photography from the hands of Daguerre drew his most thoughtful attention. He saw its enormous possibilities and promptly began a fundamental study of its chemistry, also its physics, and its practical value. From this study came the only book he ever wrote, entitled "Photography." It passed through two editions, and was everywhere regarded as standard. Its perusal reveals

the masterful mind which prepared it. It is absolutely scientific in its discussion of the problems of photography. But, foreign scientists were first in recognising the value of Lea's efforts in this new field. They declared them to have a lasting, permanent value, in scientific photography, and that they were all fundamentally important in physico-chemical research. Indeed, these researches were genuine classics. For colloid chemistry they possessed an ever-increasing interest and value. Lea's "colloid silver" and "photo-haloids" were translated and heralded abroad as epoch-making studies. Perhaps it is somewhat of a reflection upon American chemists that the importance of these studies was first emphasised by foreign chemists. However, other American labourers in the field of chemistry had their remarkable discoveries pass unnoticed, until attention was drawn to them by the regard in which they were held by co-workers in other lands, as for example—J. Willard Gibbs and his phase rule, Robert Hare and his classic work on the electric furnace, and others.

To be the discoverer of the amorphous forms of silver is no mean distinction. When these come under the eye of chemists enthusiasm is immediately kindled, and there arises an inquiry as to their discoverer.

As remarked, few chemists knew Lea personally. He was a recluse in a certain sense, for he rarely appeared in the company of scientists or other groups of men. Quietly, unostentatiously he laboured on very independently, until his contributions to purely photographic subjects reached the number of 300, to be found on the pages of the *American Journal of Science*, to which reference has already been made.

In addition to his numerous chemical papers, Lea published many others in the domain of physics. He further elaborated certain pieces of apparatus which proved helpful in laboratory work. And thus the course of his scientific endeavour proceeded, for he was a most industrious worker in all regions of his favourite science. He was a very acute observer. He knew the literature of chemistry, both past and present. He had an intense love of truth. He always had in hand the facts upon which he based expressed opinions. His opinion was recognised as the final opinion in photographic chemistry, both in this country and in Europe. He was likewise devoted to literature, the classics and art.

For one so eminent in his science he belonged to few scientific organisations—viz.,

the Franklin Institute and the National Academy of Sciences, to which he was elected in 1895.

An accident in his laboratory, in early life, so seriously injured one of his eyes that it eventually was removed. His devoted wife read to him for many years, so that he was able to keep up his interest in the current work of scholars at home and abroad.

Carey Lea was the son of Isaac Lea, a distinguished naturalist, who served as President of the Academy of Natural Sciences in Philadelphia, and of the American Association for the Advancement of Science. It was an old Quaker family into which Carey Lea was born, August 18, 1823. He was married twice, first to his cousin, Elizabeth Lea Jaudon, and after her death to Eva Lovering. Carey Lea died March 15, 1897.

The various apparatus owned by Lea was bequeathed to the Franklin Institute in Philadelphia.

The life story of Lea is most interesting. He was, indeed, a bright star in the chemical firmament of America!

#### THE CHEMICAL INDUSTRY OF JUGO SLAVIA.

The chemical industry of Jugo Slavia cannot be said to have reached a high state of perfection. It, nevertheless, possesses possibilities of considerable dimensions.

It may be pointed out that Jugo Slavia embraces old Serbia, Montenegro, Croatia, Carniola, and Dalmatia; it is also sometimes termed the kingdom of the Serbs, Croats and Slovenes. At present there is no chemical industry outside that portion of the country which was not formerly under Austrian rule.

In this region, various pharmaceutical preparations are made from the extractions of certain plants. This is a branch of chemical industry which might easily be extended in this country, which is well suited for the cultivation of many plants used for pharmaceutical purposes. At present the industry is almost exclusively confined to the preparation of perfumes.

In the north, at Ljubljana (Laibach), the local bauxite is exploited for making aluminium sulphate and alums. The metal is also produced in a limited amount. The salts manufactured are partly exported and partly consumed locally as mordants by the small dyeworks.

A beginning has also been made in the exploitation of the natural mineral resources of this district. In 1908 a kind of company, entitled "Wocheinit," was founded for mining the bauxite. This society holds all the mineral rights for the district between Bistrice and Jesenice.

During the war more than 6,000 tons of bauxite were mined. The output has since been restricted through lack of wagons, and also as a result of transport difficulties over the new frontiers.

This bauxite did not enjoy a good reputation, as it was supposed to contain a high percentage of silica, which would render its use by either wet or dry methods very difficult. The latest analyses indicate just the opposite, and it is shown that there are two kinds of bauxite. The first variety of Bohinske bauxite is said to be of the most suitable quality for the aluminium industry. It occurs in large masses on the slopes of the Julian Alps, and contains:—

Alumina .....	58-60 per cent.
Ferric oxide .....	6-10 "
Silica .....	3.5- 4.5 "
Titania .....	1- 2 "

Vogar bauxite has seams which are ten to fifteen metres thick.

The second variety of bauxite is less pure, but is very suitable for making fire-proof articles, and is found in quite separate shafts from the purer variety. It contains:

Alumina .....	52-56 per cent.
Iron oxide .....	10-16 "
Silica .....	4.5- 5.5 "
Titania .....	2- 3 "

## THE BRITISH CAST IRON RESEARCH ASSOCIATION.

### RESEARCH DEPARTMENT.

*General Research Work.*—The work in connection with the various researches is progressing to such an extent that the Director proposes to issue forthwith reports upon the various results obtained. These will be found to be of very great interest to members.

*Foundry Sand Research.*—The Bureau, in their No. 2 Bulletin, are commencing a series of articles upon Foundry Sands, which will give members some very valuable data. The object of this research is to enable standards to be established to judge one of the most important factors in the successful production of castings.

*Bulletins.*—The Bureau Bulletin No. 1 has now been issued to members, and comprises over 100 pages of very valuable information. The Research Bulletin No. 3 is in the printers' hands for early issue, and Bureau Bulletin No. 2 is also ready for the printer. Members will recognise by the receipt of these Bulletins that the Association has carried out a very large amount of useful work.

### PROBLEMS SENT IN BY MEMBERS.

During the past month members have sent in problems upon the following: Locomotive Injectors; Air compressing engine Cylinder liners; Annealing Malleable Iron; Porosity in Castings; Pan Mill Soller Rings; Mottled Castings; Spongy Trunk Slides; Cupro Nickel Ingot Moulds; Fluted Cast Iron Roll Moulds; Chilled Iron Rolls; Faulty cores in Castings; Cupola design.

### THE BUREAU AND LIBRARY.

The Bureau has been called upon to supply a large amount of data and information during the past month, and whilst there have been some cases where the required information was not in the Bureau, it was ultimately obtained from abroad, proving the great usefulness of the "Intelligence Service."

The Library Catalogue is now issued, and members will be able to use the Library to better advantage.

New books are continually being added. The following books have been sent for review in the Bulletin:—

*Causes and Prevention of Corrosion*, by A. A. Pollitt. Published by Benn Bros., Ltd., London.

*Refractories for Furnaces*, by A. B. Searle. Published by Sir Isaac Pitman & Sons, Ltd., London.

*Engineering Non-Ferrous Metals and Alloys*, by Dr. L. Aitchison and W. R. Barclay. Published by Henry Frowde and Hodder & Stoughton, London.

*British Acetylene and Welding Handbook*. Published by *The Acetylene and Welding Journal*.

### MEMBERSHIP.

During the past month further new members have been elected. These include several large firms who recognise the value of the work of the Association. The membership badge is very generally used by members on their stationery, and it is reported that this has been of great value to several of the members.

### THE GENERAL COUNCIL.

To fill a vacancy that has occurred on the Council, Mr. F. Fielding, of Messrs. Fielding & Platt, Ltd., Gloucester, has been elected to represent the counties of Gloucester, Hereford, and Monmouth. At the next annual meeting, nine members of the Council retire, eight of whom are offering themselves for re-election.

### PROPAGANDA WORK.

It has been pointed out to the Council that the advantages of membership of the Association would be better understood if meetings were held at which the officers of the Association could attend and discuss the work and objects of the Association. The Council will be glad if Ironfounding Employers' Associations or any other section of the industry would arrange meetings, when the Director of Research and the Secretary will attend. Several meetings have already been held in various districts, when good results have accrued. It has enabled the officers to discuss with the employers the needs of the industry and the absolute necessity of such an Association. After all it should be remembered that the Association is the Ironfounders' Association. It is in their power, and to their interests, to make it a great success.

### THE MALLEABLE CASTING INDUSTRY.

Unlike the malleable industry in this country, everything is being done in America to increase the production of malleable castings, and to obtain their adoption for every possible engineering use. Foremost of all, their malleable ironfounders firmly believe in research, and have practically all joined their Research Association and have standardised their products.

Secondly, they are proving to the engineer the superiority of malleable castings over drop forgings or stampings. Some time ago a complete collection of castings for railway purposes was furnished by members of the American Malleable Research Association. In addition to this exhibit a working demonstration was given to acquaint railway engineers with the properties of malleable castings. For this purpose a suitable punch press was installed, and was operated by an experienced operator. A supply of  $\frac{3}{8}$  inch cast iron plates was provided. They were punched with a  $\frac{3}{4}$  inch hole and the holes were drifted until the diameter was increased to  $1\frac{1}{2}$  inches without injury to the plate.

A torsion machine was operated to show the resistance of malleable castings to repeated strains. Bars  $1 \times \frac{3}{4}$  inch in cross section were twisted three times through  $180^\circ$ , and after each twist straightened to its original form. A further test was given in twisting a bar through  $800^\circ$  without fracture.

That malleable ironfounders in this country can produce castings equal to America is proved by some tests taken of castings made by a firm, who are members of this Association, when the tensile was 25.3 tons with elongation 14 per cent.

The Association consider these figures should be universal in the industry, if the malleable makers will join the Association and co-operate with it to obtain a general improvement in the castings the Association will be able to place before the railway and automobile engineers such reliable data as will convince them as to the advisability to use malleable work.

The Council of the Association, on their side, are doing all they can to bring back the malleable trade, but they must have the whole-hearted support of the firms themselves. The present time is the most opportune time to become members, and so prepare for the trade improvement when it arrives. Alterations in methods of production are difficult to carry out when the foundry is busy. The firms who have already joined are setting their houses in order preparatory to the busy times.

THOS. VICKERS, *Secretary*.

Central House, New St., Birmingham.

### BOARD OF TRADE ANNOUNCEMENT.

#### SAFEGUARDING OF INDUSTRIES ACT, PART I.

#### ARBITRATIONS UNDER SECTION 1 (5).:

#### ROCHELLE SALT.

The Referee has given his decision in the matter of a complaint under the above Sub-section that Rochelle Salt has been improperly included in the Lists of Articles chargeable with duty under Part I. of the Act. The Referee states that there is no evidence that Rochelle Salt is wrongly included in the Lists, and he awards that the complaint fails.

*Board of Trade,*

22nd August, 1923.

## PROTEIN REACTIONS.

(WITH SPECIAL REFERENCE TO EGG ALBUMIN).

BY R. F. HUNTER, F.C.S.

It was considered that the study of the reactions from a purely elementary qualitative point of view, of some of the commoner laboratory reagents with proteins might be a subject for investigation.

5g. of flaked egg albumin were, therefore, dissolved in 200 cc. of water as completely as possible. A white suspension was obtained. To portions of this in test tubes various reagents were added as follows:—

*Acids:*

1.—Concentrated  $H_2SO_4$ : white semi-transparent flocculent precipitate, coagulating when boiled.

2.—Co.  $HNO_3$ : pale yellow solution, precipitate pale yellow—coagulates on boiling.

3.—Co H Ce: Pale white flocculent p p, coagulation on boiling.

4.— $H_3PO_4$ : No pp, nor does warming produce pp.

5.— $H_3AsO_4$ : as for  $H_3PO_4$ .

6.— $CH_3COO H$ : No apparent action, no p p on boiling.

7.—C O O H

C O O H Indefinite.

8.—Oleic acid: pale brown: pp. on shaking.

NaO H: white flocculent pp. etc.

$NH_4OH$ .

Br Water: immediate yellow pp., coagulation on boiling.

$FeCl_3$ : Pale yellow pp.

$CuS O_4$ : Pale blue pp.

$CuSO_4 + NaO H$ , beautiful pale blue flakes.

Ni  $(NO_3)_2$ : Pale green pp.

$Am_2S$ : boiling, darkens and unpleasant odour.

$Na_2S$ : boiling produces white solid which floats on surface.

P  $(CH_3COO)_2 Pb$

$K_2 Cr O_4$ : yellow coagulation on heating.

$K Cr_2 O_7$ : orange pp.

Nitroprussiate of sodium

K C N S

K Mn  $O_4$ .

$C_2H_5OH$ : white flocc. pp., etc.

$CC_2HH_2O$ : white flocc. pp., etc.

$C_6H_6$

$C_6H_5N H_2$ : pale yellow suspension.

$C_6H_5NHNH_2$  red brown pp., red coagulation on boiling.

$C_6H_2(OH) (NO_2)_3$ , bright yellow pp. coagulation as such on boiling.

CH  $A_3$  indefinite.

The precipitation of some common elements in the presence of egg albumin was now examined.

Method: Suspension or rather dilute solution of salt studied and albumin made with water.

1.— $Pb(NO_3)_2$

HCl added—

pure white precipitate settles into two layers, solution apparently floating on suspended precipitate.

*Sulphides:*

$Hg Cl_2$ :

Sulphide first pp., orange, then separation into two layers takes place, when we have a black p.p at bottom, and transparent jelly-like suspension above layer of black sulphide.

$CuSO_4$ :

Black brown p.p appears above solution, blue-dirty green coagulated p.p appears at bottom of tube.

Bi  $(NO_3)_2$ :

Sepia precipitate and almost red brown solution. Exp. repeated with dilute solution and 1 bubble of 2S allowed to pass, red brown precipitate appears on the top, a white coagulation at bottom of tube, and between these two a pale brown solution.

$CdCl_2 - H_2S$  produces bright yellow homogeneous precipitate filling tube.

$As_2O_3$ : a pale yellow suspension from passage of  $H_2S$  and a jelly-like chrome solid floats on layer of liquid.  $Am_2S$  added which dissolves p.p. HCl addition produces peculiarly formed plastic yellow p.p. filling tube of S and  $As_2S_3$ .

$Sb Cl_3$  solution, are HCl and albumin solution:

$H_2S$ , beautiful orange red p.p. floats on white-pink solution.

$Sn Cl_2$ , deep brown p.p. floats above, almost pink solution.

$Fe_2Cl_6$  and  $AmOH$ , deep red brown flocculence on top of pale yellow liquid.

Chrome alum and  $AmOH$ :

Plastic grey green flocculence on surface of solution.

$Am_2S$  and  $MnSO_4$ :

Pale pink p.p. above solution.

$Am_2S$  and  $ZnSO_4$ , yellow colouration on top, below this olive green layer, below this dirty grey and solution below this.

Co  $(NO_3)_2$  and  $NH_4OH$ :

Blue layer above pink solution, excess  $AmOH$  produces sea-green p.p.

It was thought that a solution, or, to be more accurate, a suspension of egg albumin, might exhibit some colourations with sulphuric acid solutions of organic bases Con-

sequently this was attempted, the method being to add a small quantity of the base in its sulphonic acid form in concentrated sulphuric acid to a portion of the albumin solution in a test tube. The results were as follows:—

*Phenol*.—Indefinite reaction with clearing of suspension.

*α-Naphthol*.—Yellow solution with p.p. formation.

*β-Naphthol*.—Brown and cloudy.

*Sulphanilic Acid*.—Clear and almost golden.

*Dimethylaniline*.—Pinkish solution and flocculent precipitate.

*Salicyclic Acid*.—White flocculent p.p.

*Resorcinol*.—Yellow-green solution and p.p.

*Quinol*.—Bright golden and yellow p.p. floating.

*Pyrogalllic Acid*.—Pale-grey-pink and clear solution.

*Phenolphthalein*.—Clear sherry coloured solution.

*Fluorescein*.—Bulky olive green precipitate.

*Eosin*.—Red brown bulky p.p.

*Alizarin*.—Brilliant orange p.p.

*Anthracene*.—Grey-ochre p.p.

*Anthraquinone*.—Light grey solution.

*Aurin*.—Bright chrome solution and similar precipitate.

*Malachite Green (leuco)*.—Golden yellow clear solution.

*Benzidine*.—Pale violet precipitation floating on similar solution.

*α-Naphthyl amine*.—Indefinite.

*Diazoaminobenzene*.—Deep red solution and p.p.

*Thiocarbanilide*.—Complete white p.p.

*m-Nitraniline*.—Pale yellow-pinkish tinged p.p.

*Quinoline*.—Cloudiness.

*Pyridine*.—Cloudiness and floating of p.p.

The investigation, it will be seen, yielded nothing much worthy of note. The reactions, to put it mildly, are indefinite, which might be anticipated when one considers the complex nature of such a substance as egg albumin, particularly in solution, for in the form it probably contains a fair number of products of hydrolysis, such as complex amino acids, etc. Its effect on the precipitation of metals from their solutions by the usual methods of analyses is nothing remarkable. The only general effect apparently which one can ascribe to it is the tendency which it promotes for separation into

layers, viz., the precipitation of zinc as zinc sulphide from its sulphate solution by means of ammonium polysulphide in the presence of albumin. The effect appears to be clearly a colloidal one.

The effect of sulphonic acids of aromatic bases in sulphuric acid solution likewise does not appear to produce much worthy of comment; colour reactions were obtained, as one would expect, but nothing startling was the result.

The effects most interesting were those of coagulation and precipitation of various reagents, the work, as was stated, being qualitative in nature. This effect is not open to deduction. The quantitative study of the effect might, however, repay an investigation at a later date, but the qualitative side certainly appears to be of the nature of a failure as far as the present investigation goes.

#### STUDIES OF IRIDESCENT COLOUR, AND THE STRUCTURE PRODUCING IT.—IRIDESCENT BEETLES.

By LORD RAYLEIGH, F.R.S.

In this paper the wonderful metallic colouring of certain iridescent scaleless beetles will be considered.

Many previous writers have discussed this subject, and have taken widely divergent views as to the cause of the colours. For a summary, reference may be made to a paper by my father, the late Lord Rayleigh.\* As there set forth, the discussion turns mainly on whether the iridescent colour is due to repeated thin plates, as in the case of chlorate crystals, or whether it is of the same kind as the surface reflexion of aniline dyes. The latter view was supported by the authority of Prof. Michelson,† but I understand that he thinks that the last word has not been said on the subject.

In all cases of undoubted surface colour there is a very deep and saturated transmission of colour of complementary tint. When, however, the coloured layer of an iridescent beetle is detached by dissolving away the opaque backing and examined by transmission, it is found not to be deeply coloured, though, of course, it shows some

\* "Phil. Mag.," vol. 37, p. 98 (1919).

† "Phil. Mag.," vol. 21, p. 554 (1911).

colour, as it should do on any theory. This was the argument which, I believe, weighed most with my father, *against* the theory of surface colour, and *for* the theory of interference, or structure colour. He was not able, however, to bring forward any absolutely crucial observation, or argument, and ended by saying: "It must be confessed that much still remains to be effected towards a complete demonstration of the origin of these colours." As in the case of the chlorate crystals, I inherited the specimens which he had procured, and have obtained evidence which, it is hoped, will be found more cogent than any available hitherto. This evidence is in favour of multiple thin plates.

The only important publication on the subject which has appeared since my father's paper is one by H. Onslow,† in which the whole subject is further reviewed, and many details are given from the biological standpoint about iridescent colours of insects generally, both with and without scales. Onslow accepted the structural origin of the colours in many instances, but for the scaleless beetles here considered he reverted to the theory of surface colour. The argument on which he mainly relied was that the thickness of the colour-producing layer was too small to allow room for the structure of many parallel reflecting planes which would be required on the theory of structure colour. His estimates of the thickness of this layer were made partly in section under the microscope, partly by polishing a flat on the convex coloured surface, so as to remove the colour layer, and examining the way in which the colour fell off inwards along the normal to the boundary of the polished portion. Although I have not attempted to repeat these experiments, and cannot therefore speak from personal experience of the methods, I cannot help thinking, for reasons that will appear, that the results must be misleading.

Happening to examine the specimens in the sunlight with a direct-vision spectro-scope, I noticed that in some cases the bright region of the spectrum corresponding to the selective reflexion showed an alternation of dark and bright bands. The phenomenon is often not very conspicuous, the dark bands not being perfectly dark. Again, in some aspects of the insect the dark bands may be much more clearly seen

than in other positions. In order to see them with advantage, it is necessary to focus the surface of the insect on the slit of the spectro-scope, for otherwise the reflexions from different parts of the surface are superposed. Owing to want of uniformity in structure, the spectra from these different regions are not exactly the same, and a loss of clearness results. I have found it convenient to use a 1-inch microscopic objective to form an enlarged image of the insect on the slit. An ordinary table spectro-scope or spectrograph can be used, but the adjustments are much easier with a spectro-scope specially designed for use with the microscope. The instrument I have used is of a pattern designed by Sorby, and made by Browning. It was intended for examining absorption spectra of small objects, but serves equally well for the reflexion spectrum. A pointolite lamp is focussed on the specimen by a condenser of 3 inches focus provided with an iris diaphragm. The incident beam may be at about 20° to the axis of the microscope, and the reflected beam at about 10° from the normal to the surface of the insect passes up into the microscope. For preliminary examination the upper part of the spectro-scope is removed, leaving the slit opened wide. The field is examined with a magnifier. Any desired portion of the surface is next brought between the jaws of the slit, which is then narrowed, and the spectro-scope replaced for examining the reflexion spectrum. For photography, an additional lens and plate holder are added above the direct-vision prism.

Plate 4, fig. 1, shows a spectrum by reflexion from the beetle called *Pelidnota sumptuosa*. The angle of incidence was about 22½°, and the portion of the insect in the field was a strip which runs along the (right) side of the wing case; this coloured strip lay in the plane of incidence, and at the angle above mentioned it gave a golden yellow reflexion of great brilliancy.

The position of the insect was adjusted so that the image of this golden band lay along the slit of the spectro-scope. For determining wave-lengths the helium lines and green mercury line were put on as a comparison spectrum. It will be seen that the spectrum of the beetle consists of a strong central maximum intensity at about wave-length 6002, bordered on either side by subordinate maxima. The photographed appearance is very similar to the diffraction pattern produced by a rectangular aper-

† "Phil. Trans.," B, vol. 211 (1920).



ture, as when a distant linear source of light is examined through a telescope with a slit limiting the object glass. And although there are, of course, important differences, there is also, according to the view here taken, more than a superficial analogy between the two cases. In the case of the diffraction pattern, the bright centre corresponds to the place in the focal plane when the vibrations from the various elementary strips of the aperture are all in the same phase. If we move away laterally from this position there will be less complete agreement, and a position is eventually reached when the phases range over a complete period, and there will be zero intensity. This corresponds to the first minimum. Beyond this, there will be a certain measure of recovery until a further position, when the phases range over two complete periods. This is the second minimum, and so on. All this is repeated on the other side of the centre. In this case the light may be regarded as monochromatic; and, so far as it may not be so, the phenomena are made more complex by chromatic effects.

To pass now to the present case. Suppose that instead of a change of optical distance among the component vibrations as we pass away from the centre of the field, we have a change of wave-length. This will equally produce a discrepancy among the phases which were originally in agreement, and eventually zero intensity will be reached at the place where the phases range over a complete period. Further on there will be a second minimum, where the phases range over two complete periods.

Now this is exactly what occurs as we pass along the spectrum from the position where the phases of the waves reflected from all the parallel planes are in agreement. To state the matter quantitatively. Let there be  $n$  strata. If we neglect the effects of dispersion in the passage of light through the strata, then the whole relative retardation for rays reflected at a given incidence from the extreme planes of the system is a fixed linear quantity,  $l$ , independent of the wave-length. If we suppose, further, that the deflexion is of the first order, we have, at the centre of the system,  $\lambda_0$ , when the reflexion is a maximum,

$$l = n\lambda_0$$

at the first minimum on the red side  $\lambda_1$ ,

$$l = (n-1)\lambda_1,$$

and at the first minimum  $\lambda_1$  on the violet side

$$l = (n+1)\lambda_1^{-1}.$$

Similarly for the second minima we have  $l = (n-2)\lambda_2$  and  $l = (n+2)\lambda_2^{-1}$  so that the distance in angstroms between the first minima is

$$\frac{1}{n-1} + \frac{1}{n+1} \lambda_0,$$

and between the second minima

$$\frac{1}{n-2} + \frac{1}{n+2} \lambda_0.$$

If  $n$  is large, these distances become

$$\frac{2}{n} \lambda_0 \text{ and } \frac{4}{n} \lambda_0 \text{ respectively. Applying this}$$

to the actual case, we find from the measured spectrum that the first minima are at wave-lengths 6215 and 5790; difference 425 Å. The second minima are at 6460 and 5592; difference 868 Å; sensibly double the distance of the first minima.

Taking the central wave-length as  $\lambda$  6002, we get

$$n = 34.$$

The observed appearances are therefore explained in detail, not only as regards the central maximum, but also as regards the lateral subordinate maxima, by assuming the existence of thirty-four strata, which are situated at distances apart comparable with half wave-length in the chitinous material. This particular reflexion shows a much narrower band in the spectrum than any other I have met with, and it is the only case where the subordinate maxima can be well made out; but these are almost certainly differences of degree. This case requires a much larger number of reflecting planes than most others to explain the more nearly monochromatic character of the reflexion, and they are probably more evenly spaced than usual. Unevenness of spacing would, of course, obliterate the subordinate maxima, just as bad figure in a telescope objective tends to obliterate the diffraction rings round the image of a star.

Bands quite similar to Plate 4, fig. 1, may be observed if a good Lippmann photograph of the spectrum is examined by reflexion in direct sunlight with a pocket spectroscope. The broad central maximum, with the lateral maxima, are quite well seen, just as in the beetle.

The question now arises, can these bands be explained with any degree of plausibility as resulting from surface reflexion? It is certainly by no means impossible to obtain a surface reflexion showing a banded spectrum. Crystals of potassium permangan-

ate give a reflexion showing such bands. These bands, however, are complementary to the bands of the absorption spectrum.\* This in itself suggests that their position should be independent of the angle of incidence, and, in fact, I have not been able to observe that their position changed at all when the incidence was varied from nearly normal to about  $45^\circ$ .†

The reflexion bands shown in Plate 4, fig. 1, vary considerably as regards their position in the spectrum. This may be seen from their marked inclination to the lines of the comparison spectrum. As we pass from one part of the insect to another, the bands shift. This may result partly from change of obliquity, but I believe more from change of structure. Neither of these causes would be expected to act if the spectrum were kindred to that shown by potassium permanganate, for, as we have seen, the permanganate bands only shift under extreme variations of incidence, and we cannot well admit a progressive variation in the chemical nature of the reflecting substance itself. To postulate a large number of different chemical substances giving bands in different positions of the spectrum would be to place an intolerable burden on the theory of surface reflexion as the cause of the bands.

Moreover, the broad central band with lateral maxima conforms exactly to the requirements of the theory of multiple re-

\* See Stokes, "Phil. Mag.," vol. 6, p. 398 (1853), or "Mathematical and Physical Papers," vol. 4, p. 47.

† Beyond this point the bands are rather difficult to make out, but as was shown by Stokes, they can be brought into view by polarising the incident light perpendicularly to the plane of incidence. Introducing a nicol to do this, I have observed that at an incidence of  $70^\circ$  there is a slight shift of the bands, amounting to about 80 A. or say one-third of the width of a band as compared with the position of the bands at small incidence, or in the absorption spectrum of the solution. This displacement is towards the violet, in the same direction therefrom as the bands due to interference, but relatively very small in amount. I have only made a few casual observations on the subject. It deserves to be pursued more closely. The existence of the displacement was confirmed by photographing the spectra along with a comparison spectrum.

flexion from thin plates. On the other hand, so far as I know, there is no absorption spectrum or surface reflexion spectrum having these features.

When it is permissible to sacrifice the specimen, I have found it convenient to cut a small piece about 1 mm. square, and to mount it on the microscope stage on a special holder, which allows the piece to be rotated in its own plane, and also about an axis which lies in that plane. The specimen can then readily be brought to a position which shows the spectra to advantage.

I have examined in this way, one of the golden beetles, *Callodus parvulus*, which shows a remarkable spectrum of bands (Plate 4, fig. 2). These are most pronounced at the red end of the spectrum, and come out more distinctly when the condenser iris is narrowed to a few millimetres, so as to define more precisely the angle at which the incident rays fall upon the specimen.

If the spectroscope is replaced by an ordinary eye-piece, it can be seen that the bright reflexion from a given small area on the specimen persists when the specimen is rotated over as much as  $10^\circ$  of arc. In this observation the incident pencil was very narrow.

The surface of the insect appears to be divided up into a large number of areas which differ somewhat in structure, each giving a slightly different spectrum from its neighbours. Thus, the spectrum is divided vertically into a number of strips differing from one another as to the exact position of the dark spectral bands. The photograph as reproduced has a vertical magnification of about ninety times. It may be inferred that the areas on the insect have linear dimensions of about  $10 \mu$ , and it appears that the wide angular range of reflexion is due to the small size of the optically continuous reflecting areas. The case is in this respect similar to that already encountered in the case of labradorite.\* It may be that the absence of a definite polarising angle is explicable in the same way.

The bands in this spectrum are to be accounted for generally in the same way as the bands seen in certain chlorate crystals of complex structure.† It is necessary to postulate a group of planes giving a spectrum band limited to the red region, and

\* "Roy. Soc. Proc.," A, vol. 103, p. 34 (1923).

† "Roy. Soc. Proc.," A, vol. 102, p. 668 (1923).

another group situated at a distance from the former which gives a reflexion extending over the yellow and green. In the red region of the spectrum where these two systems overlap, we get a series of bands resulting from comparatively high interference. The distance from one dark band to the next was measured as 151 Å., at wavelengths in the neighbourhood of 6200 Å. and for an incidence  $11^\circ$  from the normal. If these bands were regarded as due to the interference of light from two strata only, as in the case of the two surfaces of a single thin film, we should have a relative retardation of forty-one waves.

The incidence may be treated as practically normal, thus the thickness would be 20.5 waves in the chitinous material, or about  $8 \mu$ . In the actual case the two interfering beams are regarded as coming not from single surfaces but from two groups each consisting of several planes. The distance between these two groups is the distance calculated above as  $8 \mu$ .

This is a much longer distance than the estimate found by Onslow from his polishing experiments on closely allied beetles, which gave him  $0.5 \mu$  only for the whole thickness of the layer concerned in producing colour. If his estimate were accepted, the theory of interference for these bands in the spectrum would have to be abandoned.

I cannot think that any one who will examine with a pocket spectroscope the bands produced by reflexion from a piece of mica  $1/100$  mm. thick will be willing to admit that the bands from *Callodus parvulus*, here reproduced (Plate 4, fig. 2), are essentially different in origin. I think, too, that a comparison of Plate 4, fig. 1 (*Pelidnota sumptuosa*), with the bands seen when a Lippmann film is examined with a small spectroscope in strong sunlight will irresistibly lead to the conclusion that the origin is similar in each case, and that the beetle, like the Lippmann film, shows reflexion from numerous planes, uniformly spaced.

#### SUMMARY.

It is shown that some of the iridescent beetles which have striking metallic colours show band systems in the spectrum of the reflected light. Two such spectra are reproduced.

The first, from *Pelidnota sumptuosa*, shows a central maximum, bordered on either side by subordinate maxima in exactly the way that reflexion from a quite uniformly spaced assemblage of thin plates

would require. The number of planes calculated to be required in this case is no less than thirty-four. A Lippmann film shows a similar spectrum.

The second spectrum is from one of the golden beetles, *Callodus parvulus*. The bands are accounted for on the supposition of two assemblages, each consisting of several reflecting planes, the distances between the assemblages being about  $8 \mu$ . This would result in a series of equally spaced bands over a limited range of the spectrum, as observed.

The possibility of either of these spectra being produced on the alternative theory of surface reflexion is discussed, and is found to require a number of special suppositions, which seem very difficult of acceptance.

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#### LABORATORY EXPERIMENTS ON THE EXTRACTION OF MESOTHORIUM FROM MONAZITE SAND.

BY HERMAN SCHLUNDT.\*

In his paper on the chemistry of mesothorium, Soddy described several experiments on the separation of mesothorium from monazite sand. In one experiment, 800 grams of monazite sand were decomposed by heating with twice its weight of concentrated sulphuric acid to which about 0.1 per cent. of barium carbonate had been added before heating. The product was stirred with cold water, and the muddy liquor obtained was decanted from the unattacked ingredients in the sand. The sediment obtained from the muddy solution contained practically all the mesothorium and radium in the monazite. The sediment from 800 grams of monazite weighed 14.5 grams and contained practically the whole of the material. The unattacked sand retained 8 per cent. of the material. A further precipitation of 1.6 grams of barium sulphate formed in the clear monazite solution possessed a small initial activity, due to regenerated thorium X only, which decayed almost completely in the course of a month. Soddy estimated that less than 5 per cent. of the mesothorium was present in the solution. The presence of thorium X in the precipitate of

\* From a paper on Mesothorium, published by the Department of the Interior, Bureau of Mines, Washington.

barium sulphate and the absence of mesothorium are regarded as clear evidence that practically the whole of the mesothorium can be separated from monazite by this method. Measurements were made by the gamma-ray method both of the original material and of the sediments. The gamma activity of the main sediment fell to 57 per cent. of its maximum value in the course of a month, as the effect of the decay of thorium X exceeded the increase due to the generation of radium C.

Soddy's procedure for extracting mesothorium was repeated in several experiments with 500 grams of monazite sand containing 6.54 per cent. of thorium oxide. One gram of barium chloride was added to the samples, before heating the sand with twice its weight of concentrated sulphuric acid. Four per cent. of the acid boiled off during cooking. The resulting paste after cooling was stirred up with 8 litres of cold water, and the muddy liquor slimed off. The unattacked sand was stirred up with another litre of water, and this liquor was decanted off and combined with the larger volume, thus making a solution containing about 10 per cent. sulphuric acid. The sediment from this solution had a dry weight of 6.2 grams, the unattacked sand 46.2 grams. In the course of several days the acid liquor gradually gelatinised on account of the partial separation of thorium as phosphate.

As the measuring instruments were not sensitive enough for accurate measurements of the gamma radiation of monazite sand, the recovery of mesothorium and the losses were obtained by making radium determinations in the monazite, the sediment bearing the mesothorium and radium, the unattacked sand, and the liquors. The radium determinations were made by the emanation method. From the sand, the unattacked residue, and the concentrate bearing the mesothorium and radium, the emanation was separated by boiling suitable samples of these materials with concentrated sulphuric acid, collecting the emanation thus liberated quantitatively, and measuring it electroscopically in calibrated air-tight electroscopes.

As the liquors coagulate upon boiling owing to the separation of thorium phosphate, it was necessary, in order to hold the thorium in solution, to acidify the liquors more; for this purpose concentrated hydrochloric acid was used. The emanation could then be separated quantitatively

by boiling, as in the quantitative determination of radium emanation present in natural waters.

The radium content of the sample of monazite sand used, containing 6.54 per cent. thorium oxide, was found to be  $7.98 \times 10^{-10}$  grams per gram when the determinations were made by decomposing the sand with concentrate sulphuric acid, and  $8.21 \times 10^{-10}$  grains when the radium determinations were made by fusion of the finely ground samples to which a little barium salt had been added with mixed alkali carbonates followed by estimation of radium directly in the refined barium sulphate.

The radium retained in the unattacked sands was to be 6.5 per cent. by the sulphuric acid method, and 7.4 per cent. by the method involving fusion with mixed carbonates of sodium and potassium. These results confirm the loss of about 8 per cent. reported by Soddy.

In the liquors were found 5.6 per cent. of the radium, making a total loss of about 12 per cent. In the radium-mesothorium bearing concentrate, 84 per cent. of the radium in the ore charge was recovered, leaving 4 per cent. unaccounted for.

#### PLANT EXPERIMENTS ON THE EXTRACTION OF MESOTHORIUM FROM BRAZILIAN MONAZITE.

No experiments were conducted on a plant scale to ascertain whether corresponding recoveries of mesothorium could be duplicated. As already stated, in the plant runs the mesothorium-bearing concentrate was separated at a later stage of operation. The intermediate stages include several treatments where rather large volumes of liquor are decanted off, therefore it is not surprising that the recovery of mesothorium falls to 65 per cent. as a result of mechanical losses of barium sulphate in these operations. The successive treatments of crude thorium phosphate eliminate nearly all of the phosphoric acid, and when the thorium chloride solution is finally obtained, a black slimy residue remains which bears the active barium sulphate.

After the residue had been washed twice with water by decantation, it was transferred to a stoneware suction filter and given another washing or two with hot water. Before analytical work on it was begun, the residue was dried for several days in steam kettles or on hot plates. At this stage the residue consisted of small, greyish black lumps having the texture of

rather low-grade graphite. This product was then pulverised to pass through a 20-mesh sieve by means of a disc pulveriser, after which it was carefully composited by quartering. The product is termed in this paper the crude concentrate of mesothorium. Duplicate samples of 500 grams each were set aside for analytical determinations of barium, lead, and radium, and for gamma-ray measurements. These samples also served in part for the laboratory experiments on the preparation of refined concentrates, which are described in a later section.

From the data summarised in Table 7, it was concluded that the addition of 1 pound of barium chloride to 400 pounds of ore, instead of 1 to 200 pounds, does not reduce the percentage recovery of mesothorium in the crude concentrate. In later runs, it was found that the addition of one-fifth of 1 per cent. of barium chloride crystals to the ore charge was sufficient to protect the mesothorium. The crude concentrate obtained when the smaller amount of barium was added, generally contained a little more than 1 milligram of gamma-ray activity per kilogram of weight.

The factor for the conversion of pure barium chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  into barium sulphate is 0.955. In the first plant run, the crystals of barium chloride added gave 91.15 per cent. of their weight of barium sulphate. In the second run, the factor was 0.9376. These factors were used in calculating the quantities of barium sulphate that resulted from the quantities of chloride added in the respective runs.

A complete analysis of the crude concentrates was not attempted. The analytical data obtained clearly show that the concentrates are complex mixtures, and in comparison with the "First sulphates" of radium-barium separated in the recovery of radium from carnotite ores, they are of low grade in barium content. By qualitative tests it was found that the crude concentrates were practically free from silica, but that 1 to 2 per cent. of phosphoric acid was still present. A small amount of thorium was also retained; lead was also present—some of it soluble and some insoluble in water. The source of the graphite and amorphous carbon present Mr. Gulbrandsen traced to the iron pots in which the sand was cooked with sulphuric acid. In the early plant runs the quantity of carbon present in the crude concentrate was more than was required to reduce the barium sul-

phate to sulphide. Some lead chloride could be extracted from the concentrate by digestion with hot water. By far the larger proportion of the lead was present as sulphate. Its amount varied considerably in different concentrates. From the concentrate obtained in plant run No. 2, nearly 5 per cent. of lead chloride was extracted by successive treatments with hot water. After the removal of the lead chloride from this concentrate, a determination of lead showed that an additional 15 per cent. of lead sulphate remained in the concentrate. The percentage of barium sulphate present in four different lots of concentrate analysed ranged from 52 per cent. in run No. 1 to 37 per cent. in one of the later plant runs.

By making radium determinations on composites of the different wash liquors, it was found that the radium losses in the acid solutions amounted to 34.6 per cent. in run No. 1 and only 20.2 per cent. in run No. 2. No explanation for this marked difference was evident. The losses in the alkaline liquors were relatively low—5.7 per cent. in No. 1 and 4.5 per cent. in No. 2.

*(To be continued.)*

## EMPIRE CANCER CAMPAIGN.

### APPEAL FOR VOLUNTARY WORKERS— BEREAVED FATHER'S SUGGESTION.

The British Red Cross Society, which is organising the appeal for the British Empire Cancer Campaign (which aims at raising £1,000,000 for Cancer Research) is appealing for voluntary workers who will assist in the collection of funds.

From the Headquarters of the Society, 19, Berkeley Street, W.1, pamphlets and leaflets advertising the aims of the campaign, books of sixpenny and shilling stamps to be sold for the benefit of the campaign, and posters designed for the purpose of advertising local fetes, concerts, etc., held in the interests of the campaign may now be obtained on application. Local organisers willing to assist the campaign may also obtain literature, stamps and posters through the medium of the local branch of the British Red Cross Society.

A valuable suggestion has been made by Mr. Reuben Wood, of Sheffield, who recently suffered the loss of his son through cancer. Mr. Wood, reading the appeal issued in May by the promoters of the

British Empire Cancer Campaign, at once wrote to the headquarters of the campaign, expressing his wish to make a collection on its behalf as a tribute to the memory of his son. He was then put into touch with the local director of the British Red Cross Society, and with the help of the local organisation was able to collect £38 9s. amongst his friends within three weeks.

Mr. Wood, who is helping to increase this sum to £100, makes the suggestion that all who have suffered a bereavement through cancer should follow his example and take active part in helping the work of the crusade which has been formed to fight the most terrible of all diseases.

When it is realised that cancer was responsible in 1921 for the loss of more than 45,000 valuable lives, and that this most cruel of all plagues is taking a steadily increasing toll of life, it is hoped that the example set by Mr. Wood will be followed in every town and village in the United Kingdom, until the sum of £1,000,000 is realised as the national contribution to the fighting fund which is to stand between the community and the advance of this disease.

#### NOTICES OF BOOKS.

*The Structure of the Atom*, by E. N. DA C. ANDRADE, D.Sc. (London), Ph.D. (Heidelberg). Pp. XIV. + 314. London: Messrs. Bell & Sons, Ltd., York House, Portugal Street, W.C.2. 1923. 16s. net.

Interest in scientific matters is not diminished by sharp conflicts in theory, for well-established ideas when in fundamental opposition stimulate interest and speculation; and one is always keenly interested in watching the developments in such cases. It is natural to expect that the true or more complete theory will remove the features in conflict and co-ordinate the otherwise discordant data.

At the present time, as is well known, two theories hold the field in respect of the atom; one being the *dynamic theory* so beautifully developed by N. Bohr, A. Sommerfeld, and others; the other being the *static theory* due largely to G. N. Lewis, W. Kossel and I. Langmuir.

Before the above theories were developed it was known that some radio-active atoms emitted  $\beta$  particles, which are negative electrons, at velocities almost that of the propagation of radiation in free space. This fact speaks strongly in favour of a dynamic

atom, for how could these electrons acquire such a prodigious velocity if they were not circulating in practically closed orbits within the domain of the atom? It is true that  $\alpha$  particles, helium nuclei ( $\text{He}^{++}$ ) are also emitted in one case with a velocity as high as about 12,800 miles a second, and it has not been suggested that they describe orbits within the atom; but enormous forces, relative to the masses involved, must exist in connection with the nucleus of the atom to give effect to such velocities, as radio-active phenomena indicate.

The energy represented by the emission of fast-moving  $\alpha$  particles in the process of radio-active disintegration is greater than that of the fast-moving electrons similarly ejected, for the mass of the former is over 7,000 times greater than that of the electron. From the energy point of view, therefore, the argument supports what might be termed the tension or strain idea as against the circulation idea, but in either case enormous forces relative to the size or mass of the bodies ejected must exist.

The smallness of the electron in terms of mass, however, leads one to expect it to suffer a great activity, for we know from the kinetic theory of gases and the Brownian movement that the great concentrated energy involved demands anything but a quiescent state of affairs. One is led to believe, therefore, that the electron has an orbital activity. If it has not such an activity, then there are conditions obtaining in the atom which make it possible to store energy by tensions or strains which are exceedingly great; but the researches of Sir E. Rutherford and the studies of Bohr point so conclusively to intra-atomic spaces in which fast-revolving electrons comport themselves, that the orbit theory is the only natural one that seems possible. As is well known, Bohr has, by applying the quantum theory to the dynamics of the atom in respect of its electrons, succeeded in accounting for the emission line spectra of hydrogen and ionised helium in a most remarkable and convincing way. This theory is in such perfect accord with the quantum theory which has now a wide application in respect of all atomic radiations, including the so-called resonance radiation, that there is here something which can hardly be due to any form of coincidence of a chance character.

The orbit theory receives strong support from the investigations of Sommerfeld, for he has shown that the application of rela-

tivity to the fast-moving electrons describing elliptical orbits accounts for the fine lines observed in the spectra of hydrogen and ionised helium; and, moreover, that the principles developed by this relativity analysis can be extended to the movements of electrons in atoms of the heavy elements. In this case the L doublet observed with X-ray spectra is quantitatively accounted for by the application of relativity to electrons describing Keplerian orbits, as in the case of the hydrogen atom.

In addition to the above, the Zeeman effect and the Stark effect have been brought into line with the dynamic type of atom established by Bohr.

The evidence seems overwhelmingly in favour of electrons describing orbits round the nuclear parts of atoms, especially those which give rise to the spectrum lines, but the static octet theory developed by Lewis and Langmuir accounts for such a mass of chemical and chemico-physical data, valency phenomena in particular, that it balances in fact the mass of data co-ordinated by the dynamic theory, as already stated.

The problem is to reconcile these two most remarkable theories without destroying the essential features of either one.

Those interested in this problem will find Prof. Andrade's book worth careful study, as the subject of atomic structure is adequately treated therein. In his concluding remarks he says: "Something as to the possibility of a reconciliation between dynamical and statistical models will be expected in such a book as this, and a word on the subject will be attempted. Have we here the complete contradiction which remains a mystery for wise men and weaker brother alike?"

'Denn ein vollkommener Widerspruch,  
Bleibt gleich geheimnisvoll für Kluge wie  
für Toren.

The answer is that we have to consider not whether an electron can be at rest and in motion at the same time—I am not sufficient of a philosopher to attempt an answer to that question—but rather whether it follows that, because for certain problems electrons may be conveniently treated as if they were at rest, they cannot be in motion? In my opinion, by no means. In the very eccentric orbits of Bohr's theory, for which the azimuthal quantum number is 1, the electron visits the outer parts of the atom periodically, and must have a preponderat-

ing effect on an electron of another atom at the same time when it is furthest from its own nucleus. Thus the external loop, if I may so call it, of such an orbit may well correspond closely in its chemical effect to an electron stationary somewhere in the region of, say, the empty focus of the ellipse to which the loop is known to approximate in form. Although the electron visits the nucleus periodically this part of the orbit which is distant from the nucleus behaves as if of different quantum number to the inner part, and as if the nucleus had an effective charge different from the actual charge, as has been pointed out in Chapter XI. Hence it is not improbable that this part of the orbit may act in a special way, much like the stationary electron or localised orbit demanded by the followers of Lewis. These loops appear locally in the surface of the atom, and may be likened—to commit myself to a picture for whose crudeness apologies are due—to handles on a spherical jug. It is true that there is a slow motion of the aphelion—or apnucleon—of the orbit, but this will have no essential effect on the problem under consideration. The nature of the forces which exist between the loops of different atoms may be electrostatic or magnetic—we need not here offer an opinion. We are more justified in considering the loops as if they were actual attachments to the atom, in that Bohr often speaks of his orbits rather as if they were actual pipes or conduits than as if they were mere paths traced out by an electron. I do not mean for a moment to suggest that this is more than a method of drawing attention to the supreme importance of the form of the orbit." To continue—

"We can also, of course, consider an electron to be shared without it necessarily being at rest. It seems, on general grounds—which are admittedly often deceptive—quite possible that one electron may pass from the orbit of one atom to an orbit of another atom, describing either a figure of 8 orbit, including a nucleus in each loop, or an approximately elliptical orbit of larger dimensions, including two nuclei within it. A conception of electron-sharing may be reconciled with a dynamical atom."

Referring to Meitner's model for radioactive nuclei, page 116, we think that the statements in this connection could be made clearer to advantage.

Bauxite is an ore of great importance in certain industries. For example, when it is fused in a special electric furnace, crystals of aluminium oxide are formed which are extremely hard, the diamond being only slightly harder. This is known under the registered trade name as Alundum. Alundum, besides being used for the well-known abrasive wheels for grinding and finishing materials in the course of manufacture, is used in another form for stair treads, as for example on tramway cars, or in railway stations. It is used also for danger places in factories where slipping must be prevented. It is quite acid resisting, and can be used in chemical works' floors. Clay is used as a binder to form the alundum tiles, wheels, etc.



THIS list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Latest Patent Applications.*

- 20385—Gaillard, E. A.—Manufacture of sulphuric acid. Aug. 10.  
 20132—Jucker & Co., Chemische Fabrik.—Recovering chromic salts from residues. Aug. 7.  
*Specifications Published this Week.*  
 201231—Merrill Co.—Process of precipitating metals from solutions.  
 201302—Farbwerke vorm. Meister, Lucius & Bruning.—Manufacture of a complex amino-argentomercaptobenzene-carboxylic acid.  
 185728—Etablissements Poulenc Freres.—Process for the commercial preparation of amino-phenyl-arsenic acids and of their derivatives.  
 201488—Vains, A. R. D.—Continuous chlorination of ligno and pectro-cellulose by nascent chlorine for the purpose of obtaining pure cellulose.  
 197932—Pereira, H.—Process for manufacturing a dye from dioxyperylene.  
*Abstract Published this Week.*  
 199154—Isatine arylides, Stephan C., of Altona, Germany.

*Isatine...-arylides* are isolated from their solutions in sulphuric acid as sulphurous acid compounds by treatment with ammonium sulphite or bisulphite in quantity corresponding with the whole sulphuric acid content; preferably the sulphuric acid solution is introduced into the sulphite solution in the form of a spray. Ammonium sulphate is recovered as a by-product, and the escaping sulphur dioxide is absorbed in ammonia to produce sulphite again. Examples are given in which the reaction product (containing isatine anilide) of example III. of Specification 15497/99 is allowed to react with solutions of ammonium sulphite or bisulphite, the isatine anilide sulphurous acid compound being precipitated.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

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# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3308.

## THE QUANTUM THEORY.

By R. F. HUNTER, F.C.S.

In a recent lecture delivered before the Chemical Society of the Royal College of Science, entitled: "Some Aspects of the Quantum Theory," Dr. C. K. Ingold, D.Sc., F.I.C., remarked that the quantum theory is less an attempt to explain than a focusing of all difficulties into one. This is very true, and it might be of some interest to us as chemists to consider, firstly, the nature of the quantum theory, and, secondly, its application in Chemistry; for the theory, though now regarded as a destined branch of Physical Chemistry, or rather Chemical Physics, is one of considerable importance to us as chemists, mainly because of its close connection, or rather interdependence with the Bohr theory of the atom, and we fear has been too long regarded in the light of a piece of mathematical physics, and its application in chemistry as being almost of the nature of trespassing of chemists in a field which is one of the most sacred domains of mathematical physics, almost as sacred as that of the theory of relativity. There would appear, therefore, no necessity to apologise for a brief elementary, and, as far as can be non-mathematical review such as this, in a chemical journal. It will of course first be necessary to run over briefly in a rough way, some of the considerations of mathematical physics, such as the question of statistical mechanics.

### ENTROPY & THERMODYNAMIC PROBABILITY, Etc.

If we have  $N_a$  molecules of hydrogen in a given space  $v$  and  $N_p$  of oxygen in a space  $v$  Then it can be shown that if we require 2 molecules of hydrogen to combine with one of oxygen, the chance of this occurrence is given by the expression:

$$\left( \frac{N_a}{N_a + N_p} \right)^2 \frac{N_p}{N_a + N_p}$$

and the rate of collision will obviously be given by an expression:

$R = \text{Rate of Collision} = K. C_a^2 C_p$ ,  
where  $R$  is a constant and  $C_a$  and  $C_p$  the concentrations.

The above is a simple application of the

laws of mathematical probability to the kinetic theory of gases.

We next consider the question of entropy and thermodynamic probability, and the relation can be shown to be of form

$$\text{Entropy} \propto \log_e (\text{Probability})$$

or  $S = k. \log_e W.$

to be more general

$$S = k \log_e W + \text{constant.}$$

By means of Boltzmann's expression,

$$S = k N \log_e u + k N \log_e v + k.$$

where  $U$  is internal energy of our system.

$R$  being defined as above;

$N$  = Number of molecules in system being a constant.

We can arrive at

$$\frac{\delta S}{\delta T} = \frac{1}{T} \frac{\delta U}{\delta T}, \quad \frac{\delta S}{\delta T} = \frac{3}{2} k N. \quad \frac{\delta U}{\delta T}$$

$$\text{hence } U = \frac{3}{2} k N.T.$$

But we know that the total kinetic energy of molecules of a gm molecule to be

$$\frac{3}{2} R T \text{ in case of monoatomic gas}$$

$$\text{then } U = \frac{3}{2} R.T.$$

and we arrive at  $N.K. = R.$

where  $R$  is gas constant per molecule, and

$$\text{for a perfect gas } \frac{3}{2} R = C_v, \text{ } C_v \text{ being gm}$$

molecular heat at constant volume, and hence our equation for monoatomic gas, becomes

$$S = C_v. \log T + R \log v + K$$

$S = \text{entropy of a gm molecule.}$

We now come to the question of equipartition of energy:

We consider a molecule of gas, to have, firstly, energy of translation; secondly, energy of vibrations; and thirdly, energy of rotation. The molecular rotations being ascribed to collisions with other molecules, and quite distinguished from atomic vibrations. Instead of molecular rotation we might have precessional vibrations. Now, in the case of diatomic molecules, we have three degrees of freedom due to translation, one in respect to linear, and two in respect to molecular rotation: six in all.

Regarding rotation as impossible and substituting precessional vibrations corresponding to degrees of freedom, again we have six in all. Now

$$\frac{1}{3} \mu v^2 = R T = \frac{1}{3} N \cdot \mu v^2$$

$$\text{KE of gn. mol.} = \frac{3}{2} R T.$$

Hence, since gas molecule has three degrees of freedom in virtue of translation, applying equipartition principle, we obtain each degree of freedom possesses

$$\text{KE} = \frac{1}{2} RT.$$

It can be shown by application of elementary mechanics that the potential energy of a particle in circular vibration is equal to the KE of vibration.

Hence we arrive at the conclusion that for a diatomic molecule, provided the law of equipartition holds, and provided that all degrees of freedom are equally effective:

$$\text{The total energy} = \frac{7}{2} RT.$$

Also  $R = 2$  cal. ap.

Therefore Energy = 7 cal.

But the molecular heat of diatomic gas varies with temperature in a way unaccounted for by equipartition principle

Where  $\frac{C_p}{C_v} = Y$  Then of  $n =$  No. of degrees of freedom of the Gas molecule

$$Y = 1 + \frac{2}{n}$$

and in a diatomic gas  $Y = 1.4 \therefore n = 5$   
 $Y = 1.3 \therefore n = 7$

and further  $Y$  is not constant and varies with temperature.

The atomic heat of solids theoretically can be shown to be given by  $C_v = \frac{d}{dT} (3 RT)$   
 $= 3 R$  on the equipartition principle.

This means that the atomic heat of a monoatomic solid should be constant and independent of temperature; but we know that atomic heat of elements in a solid state is a function of temperature, and further that this, the atomic heat, is a continuous function of temperature. Clearly then, we are faced with a wide discrepancy between what is theoretical and what we know from our experimental laboratory work.

We now turn from this subject to that of Radiation.

Jeans, assuming the number of degrees of freedom possessed by the ether to be infinite, applying the principle of equipartition, showed the energy distributed itself in the normal spectrum in such a manner that the intensity corresponding to a region lies

$$\text{between, say, } \lambda \text{ \& } \lambda + d\lambda \propto \frac{\theta}{\lambda^4}$$

meaning that we should expect the energy in the spectrum to confine itself nearly entirely to the ultra-violet region, and this is far from being the case, as shown by physical measurement.

Previously it had been shown by physicists that the intensity of radiant energy from a black body in equilibrium with the body shows a maximum value for infra-red waves.

Raleigh's experimental work, in which we have

$$4 \pi k T \lambda^{-4} d\lambda$$

yields a curve with *no* maximum, but rises rapidly as  $\lambda$  decreases.

The integration of the Raleigh-Jean equation between the limits  $\lambda_0$  and  $\lambda \infty$

$$\text{gives us } \frac{4 RT}{4 \lambda_0^3}$$

This would lead us to consider that  $\frac{1}{3}$  of the total energy will be for wave length  $> 2\lambda_0$  and  $\frac{2}{3}$  between  $2\lambda_0$  &  $\lambda_0$ . Hence we should conclude that the number of degrees of freedom of ether is not by any means infinite, and is insufficient to yield an expression which would involve conception of equipartition principle, which would agree with experimental results.

To clear matters at this point, Plank put forward his quantum hypothesis of quanta, disregarding entirely the equipartition principle. He assumed that changes of energy between matter and ether cannot be continuous, but must take place in definite steps which are multiples of some small energy unit, the energy considered being a finite function of the vibration frequency concerned.

It is of interest to note at this point that Sir J. J. Thomson considered radiant energy units or "quantum" as a region of periodic disturbance travelling along a Faraday tube.

Plank laid stress on mode of absorption and of emission of radiant energy by matter. The energy radiated by one element of a black body, for instance, is partially absorbed by the elements. Each of these vibrators or resonators which constitute

material elements in question can only emit or absorb energy in certain fractions.

Plank's resonators in the infra red, we regard as charged atoms; those in the ultra violet as electrons. For the purpose of theoretical considerations Plank regards his resonator as linear, and considers only energy vibration in one direction, entailing one degree of freedom. The important point of Plank's hypothesis is that it does away with the use of the principles of equipartition of energy, and we can state his hypothesis as follows. It is necessary for the energy to attain a finite value  $e$  in order that the resonators composing the material system may be able to absorb or emit it.

Essentially, "quantum" is not a fixed and constant quantity of energy, it is, according to Plank, a function of vibration frequency, and we can express his view as the magnitude of quantum =  $h\nu$ , where  $\nu$  is vibrational frequency and  $h$  is Plank's universal constant; and further, if one considers a material system made up of molecules, atoms and electrons, such a system must possess resonators of different dimensions, and hence of different frequencies.

If we consider a system of vibrators and resonators  $N$ , and if  $M$  possess zero energy, it can be shown that we have a relation:

$$N = \frac{M}{(1 - e^{-\xi/kT})}$$

If  $\Sigma U$  is total energy of  $N$  resonators, we get:

$$\Sigma U = \frac{Ne}{e^{\xi/kT} - 1} = \frac{N h \nu}{e^{h\nu/kT} - 1}$$

and if radiation density is  $u_\nu$ :

$$\bar{U} = \frac{8\pi\nu^2}{8\pi k\nu^3} \cdot \frac{1}{e^{h\nu/kT} - 1} \quad (a)$$

and:  $u_\nu dv = \frac{1}{c^3} \cdot \frac{1}{e^{h\nu/kT} - 1} \cdot dv$ .

This is a form of Plank's radiation formula.

If space density of energy be  $E$ , and

$$\frac{\Delta E}{\Delta \lambda} = E \lambda$$

it can be shown that

$$E \lambda = \frac{8\pi ch}{\lambda^5} \cdot \frac{1}{e^{ch/\lambda kT} - 1} \quad (\beta)$$

which is the usual form of Plank's formula for distribution of energy in spectrum.

The meaning of the constant  $k$  is shown by consideration of high temperature vibration, where one has the relation

$$E \lambda = 8\pi k T \lambda^{-4}$$

The above is the account of quantum theory as it was first conceived by Plank. Plank modified it later as follows:

While emission of radiant energy is discontinuous, viz., taking place in quanta, absorption can take place continuously, this consideration giving rise to a new expression of the form:

$$\bar{U} = \frac{h\nu}{2} \left( \frac{e^{h\nu/kT} + 1}{e^{h\nu/kT} - 1} \right)$$

This brings us to Einstein's work on the calculation of specific heats of crystalline solids, and which is mainly an extension of the quantum theory.

Defining specific heat at constant volume

$$C_v = \frac{dU}{dT}$$

when  $U$  and  $T$  have usual meanings.

Consider metals, the vibrational energy of atoms about their C.G.S. (three dimensions) is to be regarded as representing the whole internal energy of the atom, and we arrive at relation:

$$3R = 6 \text{ Cal.},$$

which is approximate, and which on equipartition principle should be constant, but which we know to vary with temperature.

Using the expression

$$\bar{U} = \frac{h\nu}{e^{h\nu/kT} - 1}$$

and denoting the average vibrational energy per gn molecule as  $U$ , one arrives at

$$U = \frac{3N h \nu}{e^{h\nu/kT} - 1}$$

$$\text{Put } \frac{h}{k} = \beta_0$$

$$\text{Then } k = \frac{R}{N}$$

$$h\nu = \frac{R}{N} \beta_0 \nu$$

$$U = 3R \cdot \frac{\beta_0 \nu}{e^{\beta_0 \nu/T} - 1}$$

$$\& C_v = \left( \frac{dU}{dT} \right)_v = 3R \frac{e^{\beta_0 \nu/T} \left( \frac{\beta_0 \nu}{T} \right)^2}{(e^{\beta_0 \nu/T} - 1)^2}$$

The correction giving us  $C_v$  as a function of temperature.

(To be concluded next week.)

## A THEORY OF CHEMICAL REACTION AND REACTIVITY.

By E. C. C. BALY, C.B.E., F.R.S.

All theories of the absorption of energy by molecules, more particularly the modern radiation theories of chemical reaction, are based on the assumption that molecules are characterised by definite free periods of vibration. Further, the energy quantum theory has as its basis the additional assumption that the absorption and radiation of energy at the molecular frequencies are not continuous but discontinuous. It is a necessary *sequitur* that any radiation theory of chemical reaction developed from these two initial assumptions must be one of monochromatic radiation. It was first shown by Henri and Wurmser, and more conclusively by Langmuir, that all these theories entirely fail to explain the facts, the number of molecules that react being enormously greater than that calculated from the known amount of energy absorbed, and the resulting criticism of these monochromatic radiation theories becomes singularly cogent.

It is well known that any substance (other than black bodies) possesses the power of selectively radiating and absorbing radiant energy of definite frequencies in the infra-red, ultra-violet, and sometimes in the visible, regions of the spectrum. Moreover, the frequencies exhibited by any substance in the visible and ultra-violet are always exact integral multiples of a fundamental frequency exhibited by that substance in the short wave infra-red. Again, the fundamental short wave infra-red frequency is always an exact integral multiple of the frequencies exhibited by the substance in the long wave infra-red. This integral relationship has a most important bearing on the radiation of the energy that has been absorbed. It is obvious if a substance absorbs energy without undergoing any photo-chemical change that the whole of the energy is radiated at longer frequencies. Let it be supposed that a single molecule absorbs one quantum of energy at one of its characteristic frequencies, say in the ultra-violet, without undergoing any photochemical change. This amount of energy is radiated at the infra-red frequencies and indeed as an exact number of quanta at those frequencies. This is only rendered possible by the integral relationship between the frequencies exhibited by the molecule. The monochromatic radia-

tion theories of chemical reaction take no account of the radiation of the energy during the reaction.

It is possible to formulate a theory of absorption of energy which is based on assumptions that are different from those which are usually made. It may be assumed first that an elementary atom is characterised not by a free period of vibration but by a definite amount of energy associated with a specific physical change in the atom, such, for instance, as the shift of an electron from one orbit to another. On this assumption an atom can only gain or lose energy in terms of this unit or elementary atomic quantum of energy. A second assumption may be made that the physical change in the atom occupies a definite period of time which is the same for all atoms. The atom then becomes capable of absorbing or radiating energy of a definite frequency. It may in the third place be assumed that the elementary quanta of all the known atoms are integral multiples of a fundamental unit which very possibly is the elementary quantum of the hydrogen atom.

On the basis of these three assumptions it is possible to formulate a theory of chemical reaction which has very material advantages over the better known monochromatic theories. In the first place the theory is not monochromatic and is able to explain the serious discrepancies noted by Henri and Wurmser and by Langmuir. In the second place it appears capable of explaining the phenomena of absorption spectra, together with the integral relationships referred to above. Lastly it seems to present an interpretation of the mechanism of a reaction including the phenomenon of catalysis.

When two elementary atoms combine together energy is evolved and the simplest possible condition may be assumed, namely, that each of the two atoms contributes an equal share of the total energy lost. On the first assumption made above each atom can only lose energy in terms of its elementary quantum, and therefore the smallest amount of energy that each of the two atoms can lose is the least common integral multiple of the elementary quanta of the two. Thus, if 3.7 and 7.1 represent the elementary quanta of the two atoms, the smallest equal amounts of energy that can be evolved by the two atoms will be 71 quanta of the size 3.7 in the one case, and 37 quanta of the size 7.1 in the other. The total energy lost therefore will be  $2 \times 71$

$\times 3.7 = 525.4$ . It must be noted that this is only possible on the third assumption of the integral relationship between all elementary atomic quanta.

Further, the gain or loss of energy by the resulting molecule as a whole must be a process in which its atoms bear an equal share, and thus the smallest possible amount of energy that the above molecule can lose as a whole will be represented by the number 525.4. We arrive, therefore, at the conception of a molecular quantum, which is a multiple of the least common integral multiple of the elementary quanta of its component atoms. Just as an atom is characterised by a frequency which is established by its elementary quantum, so also will a compound molecule be characterised by a frequency established by its molecular quantum. It must be noted that a molecular quantum is not, strictly speaking, a physical entity, but only a summation of an integral number of atomic quanta. Any criticism that might be uttered against the conception of a molecular quantum as the summation of an integral number of atomic quanta, must give way before the necessity on the Planck theory of the radiation of a single quantum, absorbed by a molecule, as an integral number of smaller quanta.

Chemical reaction between atoms, therefore, consists in the joint loss of an equal amount of energy by the atoms whereby a stable molecule is produced. A very essential feature of this theory is that the atoms on combining together do not lose their individuality as absorbers or radiators of energy. The molecule will be able to absorb its molecular quantum and also quanta characteristic of each of its component atoms, and it is important to note that if the molecule specified above be exposed to radiation equal to that of one of its atoms, for example the atom with quantum of size 3.7, this atom will absorb its quanta, and when 142 of these have been absorbed the whole molecule will have gained an amount of energy equal to one molecular quantum.

For the sake of simplicity the case was considered of two atoms combining to form a binary molecule. The same argument applies to more complex molecules, but in such cases the results are not necessarily so simple. Although the molecular quantum is always a multiple of the least common integral multiple of all the atomic quanta, and although the molecule will on examination exhibit its molecular and atomic fre-

quencies, the possibility now arises of definite groups of atoms within the molecule playing their part. In this case, in addition to the molecular and atomic quanta and frequencies, there will be intra-molecular quanta and frequencies characteristic of the atomic groups. Absorption spectra observations have established the existence of all three types of frequencies, molecular, intra-molecular, and atomic, and moreover the combinations of these frequencies due to the simultaneous absorption of two or more quanta have been recognised. It is to these combined frequencies that the breadth of the so-called absorption bands is due.

The molecular frequency is usually situated in the short-wave infra-red, namely, that region lying between the wave-lengths  $10\mu$  and  $3\mu$ . The atomic frequencies lie in the very extreme infra-red, and are of the order of  $1.5 \times 10^{11}$ , which corresponds to a wave-length of  $2000\mu$ , whilst the intra-molecular frequencies lie in the region between the two. In view of the derivation of the molecular frequency it is not necessary to explain the fact that this is always an exact multiple of the smaller frequencies exhibited by the same molecule.

Up to the present nothing has been said of the origin of chemical combination, that is to say the force or affinity which attracts the atoms together in the first place. There is little doubt that the explanation of this is to be found in the electromagnetic force fields of the atom. Each atom forms the centre of an electromagnetic force field and possesses two faces which may be called positive and negative. When two atoms approach one another in such a way that their like faces come together, they will repel one another, but if their unlike faces come together they will attract one another. When two atoms attract one another in this way they are able to lose energy in common as already described, and we call the process chemical combination.

It must be remembered, however, that one face only of each atom is concerned in the chemical combination, and there remains to be considered its second or what may now be called its external face. Since the external faces of the atoms in a molecule must be of different type, it is not possible to assume that they have no influence on one another. The lines of force must condense together to form a molecular force field with the escape of energy. This process obviously is one in which the mole-

cule as a whole takes part, and therefore the energy lost must be in terms of the molecular quantum. The force field condensation therefore will take place in stages, each stage corresponding to the loss of one molecular quantum. A freshly synthesised molecule is unstable, and must lose one or more quanta by the condensation of its atomic force fields, and so must pass into one of a number of possible phases, each consecutive phase differing in energy content by one molecular quantum. It is readily shown that when the freshly synthesised molecule loses one molecular quantum it becomes endowed with a quantum which is twice the molecular quantum, and hence with a frequency which is twice the molecular frequency. In general the phase quantum and phase frequency are  $x+1$  times the molecular quantum and frequency respectively, where  $x$  is the number of molecular quanta lost in the force field condensation.

In addition, therefore, to its molecular frequency and smaller frequencies due to the atoms and groups of atoms, a molecule will exhibit a phase frequency which always lies in the visible or ultra-violet. Since this phase frequency is an integral multiple of the molecular frequency the whole of the arithmetic relations that have been proved to exist between the frequencies of a molecule are explained. Emphasis may again be laid on these relations. The phase quantum and molecular quantum are not real entities, but only summations of an integral number of atomic quanta. If a molecule absorbs one phase quantum this may be radiated either as one quantum of a less condensed phase together with an integral number of molecular or atomic quanta, which is the origin of fluorescence or phosphorescence, or entirely as an integral number of molecular or atomic quanta. Conversely a molecule may gain one or more molecular quanta on exposure to radiation of a frequency equal to one of its atomic or intra-molecular frequencies.

The molecular phases may now be considered in greater detail. The particular phase into which a freshly synthesised molecule will pass depends on two factors. In the first place it will depend on the relation between the external fields of its atoms, and in the second place it will depend on the conditions under which the molecule exists. It is evident that if the positive and negative affinities of the external atomic fields are equal and opposite, the molecular force

field condensation will proceed far with the escape of many molecular quanta. In such a case the phase formed will be characterised by a highly condensed field with its frequency situated in the extreme ultra-violet. On the other hand if the atomic fields are unequally balanced, the condensation will not proceed very far, and a balance of one type of affinity will remain uncompensated.

When large numbers of molecules are considered it must not be expected that they will all exist in one particular phase. Indeed observation shows that the most usual condition is an equilibrium between two or more phases.

Then again, it follows that it is possible to change the phase in which a molecule exists by supplying to it or taking from it one or more molecular quanta. One of the methods of doing this is by the use of a suitable solvent. The change in frequency exhibited by a molecule in the visible or ultra-violet by the use of different solvents has been observed in a great number of instances. Similar phase changes have been observed in many cases with change of temperature.

Since the chemical reactivity of atoms is a function of their force fields, so also does the reactivity of a molecule depend on its force field. From what has already been said of the formation of molecular phases it follows that the reactivities of the different phases of a given molecule will be different. The difference in the reactivity of the phases can very easily be proved.

In order, therefore, that a molecule can enter into a particular reaction it is necessary to bring it into the proper phase, and it may be said that in general this means a less condensed phase than that in which the molecule normally exists. The importance of this deduction from the present theory is manifest. It at once gives an explanation of the fact that so many reactions will not take place without energy being supplied to the molecules, and moreover, it enables us to calculate the exact increment of energy required by each molecule. This increment of energy amounts to one or more molecular quanta, depending on the initial and reactive phases. There is no method at present known of directly measuring the size of the molecular quantum, but it may be obtained by multiplying the molecular frequency, which can readily be observed, into the time factor, and for this we may use the Planck constant 6.57

$\times 10^{-27}$ . If the initial and reactive phases are known, the necessary increment of energy for one molecule may be found.

There are two methods of supplying the increment of energy required for the phase change. In the first place the molecule may be exposed directly to a source of radiant energy in the form of heat or light, and in the second place the energy may be supplied by a material catalyst. Whilst the first method may be readily understood, the action of a catalyst requires some explanation. It was pointed out above that in those cases where the external atomic fields are unequally balanced the molecular force field condensation will not proceed very far owing to the uncompensated balance of affinity of one type. If such a molecule forms an addition complex with another molecule by virtue of this uncompensated balance, there will now be nothing to prevent the force field condensation from proceeding further with the evolution of one or more molecular quanta. If the second molecule in the complex has the same infra-red frequency as the first, the one or more quanta given up by the first molecule may be absorbed by the second molecule, with the result that the latter is converted into a less condensed or more reactive phase. This explanation of the change of phase produced by a solvent can readily be put to the test of experiment. In the first place the infra-red frequencies of the two, solute and solvent, must be similar, and in the second place if the solute molecule is converted into a less condensed phase the solvent molecule must pass into a more condensed phase. It has been found that when two molecules form an addition complex, this complex does not exhibit the molecular frequencies of its two components, but a molecular frequency of its own. The mechanism for the transference of one or more molecular quanta from one molecule to the other is therefore perfect. Again, some recent investigations appear to show that in such a complex, when one component passes into a less condensed phase, the other component passes into a more condensed phase. The explanation of the effect of a solvent in changing the phase of a molecule is thus experimentally verified. It may be stated that although this explanation has been given for the particular case of a solvent and solute, it undoubtedly applies to all cases of catalysis. A catalyst may be defined as a substance which by virtue of its power of forming an addition

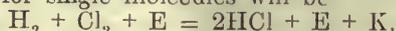
complex with the catalyte converts the latter into a less condensed and more reactive phase, itself passing into a more condensed phase.

It will be evident that the deductions made from the three original assumptions as to the existence of elementary atomic quanta lead to a radiation theory of chemical reaction, a theory which differs from the better known theories in the essential fact that it does not rest on a basis of monochromatic radiation. The deductions made from this theory may be briefly recapitulated. The existence is established of simple integral relationships between the various frequencies exhibited by a molecule and of the combination of these frequencies to form subsidiary frequencies within the absorption bands. These relationships have all been observed.

A molecule must exist in one of a number of possible phases, any two consecutive phases differing in energy content by one molecular quantum of energy. Each phase is characterised by its own phase quantum and phase frequency, and each phase is endowed with its own specific reactivity. A molecule must be brought into the appropriate phase before it can take part in a reaction. Since a molecule in the free state exists in a more condensed phase than the one desired, it is necessary to supply energy to the molecule to produce the phase change. This increment of energy is exactly equal in amount to one or more molecular quanta, the number depending upon the difference between the initial and reactive phases. The energy can be gained by the molecule on exposure to radiation of frequency equal to its atomic, intra-molecular, or phase frequency. Changes of phase produced by heat and by light have frequently been observed. The effect of temperature is due to the summation within the molecule of an integral number of atomic or intra-molecular quanta to give the one or more molecular quanta required. When the phase change is produced by the absorption of a phase quantum, the balance of energy over that required is radiated as fluorescence or phosphorescence. The increment of energy may be supplied by a material catalyst which forms an addition complex with the molecule in question. Within this complex one or more molecular quanta are given to the reactant molecule by the catalyst molecule, the former passing into a less condensed, the latter into a more condensed phase.

Mention may be made of the experimental evidence in support of this theory. The integral relationships between the frequencies exhibited by a molecule and the change of phase exhibited by a catalyst have already been dealt with. The most important confirmation of the theory is to be found in the explanation which it gives of the discrepancy observed between the actual and calculated number of reacting molecules. The better known theories make the very simple, not to say obvious, assumption that a minimum of one energy quantum is necessary to activate a single molecule. From a knowledge of the energy absorbed in any given reaction and the frequency characteristic of the reacting molecules it is easy to calculate the number of molecules which should have reacted. In general the actual number is many million times larger than the calculated number, the divergence of the observed from the calculated number being different in different cases.

These monochromatic theories, however, take no cognisance of the destination of the energy that has been absorbed. The application of the present theory will be understood more easily from a particular case which has been quantitatively studied, namely, the photochemical union of hydrogen and chlorine. As is well known, this reaction proceeds when the mixture of gases is exposed to radiation of frequency equal to that characteristic of chlorine. The equation for single molecules will be



where E is the amount of energy absorbed by the chlorine molecule, *i.e.*, one phase quantum, and K is the observed heat of reaction for the formation of two molecules of HCl. For the present purpose it is of no consequence whether the amount E is or is not the minimum amount necessary to activate a chlorine molecule. The sole point of importance is that E is exactly one phase quantum characteristic of the free chlorine molecule. During a reaction two molecules of HCl are formed and the energy E + K is radiated. This energy is radiated by the HCl at infra-red frequencies characteristic of the HCl molecule. The quantity E cannot be radiated by the chlorine, for if it were so radiated the chlorine would lose its reactivity. Now the HCl molecule has at any rate some infra-red frequencies identical with those of chlorine, and consequently the energy E + K can be re-absorbed by the surrounding Cl<sub>2</sub> molecules with the result that these become partially or wholly acti-

vated. Since in this reaction K is positive, the reaction being exothermic, the number of molecules of chlorine that react will very greatly exceed that calculated on the basis of one for every phase quantum absorbed, the excess depending upon the proportion of the energy E + K that is re-absorbed. The only condition under which observation and calculation can agree is when K is numerically equal to E and is negative, so that E + K = 0.

The proportion of the radiated energy that is re-absorbed will obviously depend on two factors, the density of the chlorine and the density of the radiation. According to the present theory, therefore, the divergence from Einstein's law of one molecule reacting per phase quantum absorbed will increase, both when the density of the chlorine is increased and when the density of the radiation is increased, or what comes to the same thing, when the intensity of the incident light is increased. It has already been proved that with constant intensity of illumination the velocity of the reaction is proportional to the square of the concentration of the chlorine. Several other instances of the increase of the divergence from Einstein's law with increase in concentration under constant illumination have been noted. It has recently been shown also that the divergence from Einstein's law increases very rapidly with increasing intensity of the illumination. Three observations of some interest were made in these latter experiments. During the first instant of illumination the reaction must obey Einstein's law, but the re-absorption of the radiated energy will at once commence with the result that the rate of the reaction with moderate intensities of light will rapidly increase up to a constant maximum depending upon the proportion that is re-absorbed. This phenomenon was observed in every case.

Since the proportion re-absorbed increases with intensity of illumination, a condition will be reached with increasing illumination when the proportion re-absorbed will be sufficient completely to activate the surrounding chlorine molecules. Under this condition the reaction once started by the absorption of a single phase quantum will pass as an explosion wave through the whole mixture. The existence of a lower limit to the intensity of the illumination necessary to cause the explosive combination of hydrogen and chlorine has long been recognised.



The third phenomenon observed is one of very great interest. If the activating source of light be cut off when the maximum rate of reaction has been reached, the reaction ceases at once, but it is very surprising how long an interval of time must elapse before the chlorine reaches its normal condition, since at least thirty minutes are required. If the light be allowed to fall on the mixture before this minimum period of rest has expired the initial rate of reaction is greater than the normal initial rate. The obvious explanation is the presence of partially activated chlorine molecules, that is to say molecules containing more than their normal number of atomic quanta, which, however, do not in the case of any one molecule amount in their sum to the increment of energy necessary for complete activation. This condition is readily understood from the present theory, and raises the possibility of two samples of the same gas apparently in thermal equilibrium with one another but having different energy contents. It is hardly necessary to point out that all the phenomena observed in the photochemical union of hydrogen and chlorine, originally foretold from the present theory and recently proved experimentally, cannot be explained by any monochromatic theory of reaction.

An extension of the principle of the re-absorption of the radiated energy may be mentioned, namely the photocatalysis of a reaction whereby a molecule is activated, when screened from rays of its characteristic frequency, by other molecules which in absorbing their own molecular quanta emit infra-red rays, these being absorbed by the first molecule. Evidently this will be possible if the two molecules have the same atoms in common. It is only necessary here to record the fact that several reactions have been successfully photocatalysed, and of these not the least interesting is the formation of formaldehyde from carbon dioxide and water in visible light in the presence of certain coloured bases such as malachite green. As is well known the characteristic frequency of carbon dioxide lies in the very extreme ultra-violet and in the absence of the photocatalyst the synthesis of formaldehyde requires radiation of that frequency.

Finally a brief reference may be made to some further observations which have not yet been published. The possibility of the existence of two samples of the same gas in apparent thermal equilibrium with one an-

other but in different molecular phases has already been mentioned. This phenomenon is somewhat strikingly exemplified by ammonia and its decomposition by an electrically heated platinum wire. With a constant current the amount of ammonia decomposed in a given time depends on the condition of the gas. When the ammonia is prepared by the very slow evaporation of the liquefied gas or by warming its concentrated aqueous solution, the amount decomposed is many times larger than when the gas is obtained by the rapid evaporation of the liquid, the temperature of the two samples and the amount of energy supplied to them being exactly the same. On standing for many hours the "inactive" ammonia tends to reach the normal condition.

Many substances are known which exist in different molecular phases in the gaseous and liquid states, and in all probability ammonia is analogous in this respect. The very rapid evaporation of the liquid will give a gas containing a greater proportion of its molecules in the more condensed phase than is normal. The result will be that a given amount of energy will decompose fewer molecules than in the case of normal ammonia.

Instances might be multiplied of the application of this theory to chemical reaction but sufficient has been said to justify the original claim that it is possible from the assumption of elementary atomic quanta to formulate a theory which accords better with the observed facts than the theories of monochromatic radiation.

(From "Transactions of the Faraday Society," Vol. XVII., Part 3.)

#### LABORATORY EXPERIMENTS ON THE EXTRACTION OF MESOTHORIUM FROM MONAZITE SAND.

By HERMAN SCHLUNDT.\*

(Continued from Page 141.)

Fully two-thirds of the combined losses in the liquors was confined to one of the acid liquors. Though the investigators were at first inclined to attribute the major portion

\* From a paper on Mesothorium, published by the Department of the Interior, Bureau of Mines, Washington.

of this loss to chemical action, later, after examination of the sediment in this liquor, it was concluded that the loss was almost entirely mechanical, barium sulphate having been carried over in the wash liquors when they were siphoned off. The loss of values in the unattacked sands appears to correspond to the weight. In the first run the tailings constituted 9.4 per cent. of the monazite sand treated, and the radium found was 8.3 per cent. In the second run the unattacked sands constituted 6.1 per cent. of the weight of the ore, and the percentage of radium found was 5.85 per cent.

In conducting the analytical work, determinations were generally made in duplicate or triplicate by at least two methods. In the estimation of radium, for example, in monazite, and the concentrates, the two methods have already been outlined. By following this plan throughout the investigation it was learned that several of the methods of analysis required modification.

The radium determinations in monazite sand gave values 5 per cent. higher when the ore was decomposed by fusion with mixed carbonates instead of sulphuric acid, therefore it was concluded that the residue that was unattacked by sulphuric acid held materials containing radium. This conclusion found confirmation in the radium determinations made on the unattacked sands by both methods. When the emanation was separated directly by boiling with concentrate sulphuric acid, the values were scarcely a third as high as those obtained by first decomposing the tailings by fusion with mixed alkali carbonates.

#### DETERMINATION OF LEAD AND BARIUM IN THE CONCENTRATE.

In the first method of analysis the lead and barium were extracted with concentrated sulphuric acid, and the recovered sulphates were then refined by fusion with mixed alkali carbonate, and finally after separation were precipitated as sulphates. As the percentages of lead and barium found in this method stand in close agreement with the results obtained by direct fusion of the concentrate with mixed alkali carbonates, confidence was gained in the method of determining radium in the concentrate, when the emanation is separated by boiling samples with concentrated sulphuric acid. The fact that lead and barium can be extracted quantitatively from the crude concentrate with concentrated sulphuric acid also suggests a possible method

of refining this product on a commercial scale.

In the analytical determinations 5-gram samples of the concentrate were boiled for 10 minutes with 120 cc. of chemically pure sulphuric acid. After cooling somewhat, the insoluble residue was filtered off on a Gooch crucible with asbestos mat, and washed twice with hot concentrate acid. From the filtrate, lead and barium were precipitated by dilution with two to three litres of water. The recovered sulphates were then refined by fusion with mixed carbonates and the washed carbonates were converted into chlorides. To separate the lead the filtrate was made barely alkaline with ammonia, and then saturated with hydrogen sulphide. In the filtrate barium was precipitated as sulphate; lead was also estimated as sulphate in the solution obtained by dissolving the precipitate of lead sulphide in dilute nitric acid.

In the other method, 5-gram samples of the crude concentrate were used directly with mixed carbonates in nickel crucibles. An insoluble residue of nearly 10 per cent. generally remained when the washed carbonates were treated with dilute hydrochloric acid. A second and third fusion, however, did not yield additional barium or lead. In the concentrate from run No. 2 the writer found 46.56 per cent. of barium sulphate by extraction with sulphuric acid and 47.26 per cent. by direct fusion with mixed carbonates. In run No. 2 the lead content of concentrate was estimated as at least 21 per cent. sulphate. This high percentage of lead sulphate in concentrate No. 2 explains an observation made subsequently in connection with experiments on refining the crude concentrate. When heated, much sulphur dioxide is liberated at about 600° C., probably as the result of the interaction of lead sulphide formed by the reduction of some of the lead sulphate by carbon, with unreduced lead sulphate.

#### REFINING OF MESOTHORIUM IN THE CRUDE CONCENTRATE.

The method finally employed for extracting the barium in the two batches of crude concentrate that was obtained in experimental runs 1 and 2, and for obtaining it in soluble form, followed closely the process used in refining the "first sulphates," produced in the extraction of radium from carnotite ores. The barium sulphate carrying the radium at a concentration of about 1 mg. kilo was intimately mixed with char-

coal, and was then reduced to sulphide at about 1000° C. The reduced product when leached with hydrochloric acid gave a solution of barium chloride, ready for further concentration of mesothorium by fractional crystallisation.

Before adopting the direct reduction method, a number of laboratory experiments were conducted with 5, 10, 50, and 100-gram samples of the crude concentrates of mesothorium-barium, with a view to securing data on other methods of possible practical value.

In outlining the methods of analysis attention was directed to the quantitative extraction of barium from the concentrate by digesting it with a large excess of concentrate sulphuric acid. In order to insure the barium being completely dissolved in the concentrate it must be boiled with at least six times its weight of acid. About 40 per cent. of the material remains unattacked. When the black residue is filtered off on a suction filter fitted with asbestos mat and washed with two portions of hot concentrate sulphuric acid, fully 95 per cent. of the barium may be recovered upon diluting the acid liquor with 10 to 15 times its volume of water. The partly refined sulphate thus obtained may be converted almost quantitatively into soluble form by one of three methods: (1) Reduction to sulphide at high temperatures by carbon; (2) conversion into carbonates by fusion in iron kettles with a mixture of sodium hydroxide, 1 part, to soda ash, 2 to 3 parts, leaching of the fused mass, washing free from sulphates, and conversion of the insoluble carbonates into chlorides—recoveries running as high as 97 per cent. were obtained by this method; (3) prolonged boiling of the refined sulphates with a concentrated solution of sodium carbonate about four times in excess of the sulphates present. With constant stirring by means of a mechanical stirrer during the digestion period, conversions as high as 92 per cent. were obtained. Methods 2 and 3 can be applied directly to the crude concentrate with equally good results. More than 20 preliminary experiments of this character were conducted with 50-gram samples of concentrate before the decision was reached to treat the main bulk of the concentrate by direct reduction with carbon as the first step in refining.

In the early reduction experiments, 500-gram charges were carried through and the amount of soluble barium determined. At first enough powdered charcoal or lamp-

black was mixed with the crude concentrate to reduce all of the barium and lead sulphates. In the course of the experiments, it was soon noted that the residue remaining after the reduced product had been leached with hydrochloric acid was nearly as bulky as the original charge. Furthermore, some experiments to determine the loss on ignition revealed the reduction of a large fraction of the sulphates. In short, it soon became evident that the admixture of graphite and amorphous carbon present in the crude concentrate was more than enough to reduce the sulphates completely. The concentrates from the two experimental runs were reduced in the technological laboratory of the United States Bureau of Mines at Golden, Colo., and later, after it was found that the concentration of mesothorium by fractional crystallisation of the chlorides and bromides proceeded normally, two other batches of concentrates weighing, respectively, 349 and 745 pounds,\* were given this treatment in the plant of the Welsbach Co. The reductions were carried out in graphite crucibles with 30-pound charges heated 4 to 5 hours at 1100° C. and sometimes even higher. The recovery of values and the losses in the various products were investigated throughout the experiments by two distinct methods of analysis: The chemical method involving determinations of barium, and the radioactive method, embracing comparisons of gamma-ray activities and determination of radium by the emanation method.

#### THE PULP AND PAPER INDUSTRY OF CANADA.

One of the outstanding features of Canada's manufacture and commerce in the last two decades has been the rapid growth of the pulp and paper industry. This growth resulted primarily from the juxtaposition of large supplies of suitable pulpwood timber and cheap electrical energy. Large areas of coniferous forest traversed by rushing streams and rivers, providing water power, form the basis upon which the industry has been built up.

Forty years ago there were only 5 mills in operation in Canada; to-day there are

\* Experimental data are given for a part of this concentrate, 179.3 kg., in Table 8.

more than 120, consuming over two million cords of pulpwood per annum and using hydro-power to the extent of 637,000 h.p. In 1921 the capital invested exceeded 380 million dollars, while the value of products was over two hundred million dollars.

#### EXPORT TRADE.

From the point of view of the Dominion's export trade, the pulp and paper industry holds a position that is second only to that of agriculture. The figures given below give a comparison of the exports of the products (animal and vegetable) of Canada's farms with pulp and paper exports, for the years indicated:—

Year	Farm Produce (Millions of dollars)	Pulp and Paper
1914 .....	245.9	19.1
1923 .....	467.1	122.6

The rapid progress of the pulp and paper industry as a contributor to Canada's trade is shown in the following table of the exports of pulp and paper for the past twelve years:—

Year	Paper prod. (Millions of dollars)	Wood-pulp	Total
1912 .....	3.9	5.1	9.0
1913 .....	6.3	5.5	11.8
1914 .....	12.7	6.4	19.1
1915 .....	15.5	9.3	24.8
1916 .....	20.0	10.4	30.4
1917 .....	26.1	20.4	46.5
1918 .....	37.7	25.6	63.3
1919 .....	47.9	34.7	82.6
1920 .....	63.2	41.4	104.6
1921 .....	92.1	71.6	163.7
1922 .....	69.5	35.9	105.4
1923 .....	79.6	43.0	122.6

The great fluctuations in price in the years 1920-22 affected to some extent the generally steady increase in production. Since that period, however, it will be noted that the increase has been resumed.

Figures of the total production of wood-pulp are available for a number of years back. Those for newsprint paper (which forms from 80 to 85 per cent. of the total) are available for certain years, and these tell the same story of progress as the exports.

Year	Wood-pulp (tons)	Newsprint (tons)
1917 .....	1,464,308	689,847
1919 .....	1,716,089	794,567
1921 .....	1,549,082	805,114

#### SUBSIDIARY INDUSTRIES.

Although large supplies of pulpwood and lime are readily available in Canada, the pulp and paper mills are at present importers of many of the raw materials entering into the manufacture of chemical pulps and paper. In the fiscal year ending March 31, 1923, sulphur valued at \$1,673,662 was imported chiefly from the extensive Louisiana sulphur deposits; of this amount, about three-fifths was used in the pulp and paper industry. Sulphur can be produced from the domestic deposits of pyrites, but under present conditions cannot compete with the imported brimstone. Imports of alum and salt cakes amounted to over \$1,000,000, of which seven-tenths was used in the manufacture of kraft pulp. Canada's dependence upon outside sources for this chemical will probably diminish as the sodium sulphate deposits of the Prairie Provinces are gradually developed. Again, though kaolin or China clay is produced in small quantities in the province of Quebec the value of imported clay used in the pulp and paper industry amounts to about \$200,000 yearly. Other products which are imported include resin, alum, pulp-stones, acid proof refractories, and soapstone linings. Some of these are being produced in Canada and as the pulp and paper industry grows, a large enough market will become available to warrant the development of Canada's resources for these commodities.

These facts are another reminder of the importance of Canada's forests and of the need for the adoption of all possible measures for their conservation.

#### GENERAL NOTES.

##### AIRCRAFT APPRENTICES FOR THE ROYAL AIR FORCE.

The Air Ministry announces:—

The decision of the Government to increase the strength of the Royal Air Force for Home Defence purposes necessitates the engagement of aircraft apprentices, who will be trained as skilled craftsmen, in largely increased numbers.

For the entry in January next, approximately 950 boys of a good class will be required. The selection to fill these vacancies will be made on the results of two competitive examinations, which are conducted re-

spectively by the Civil Service Commissioners and by the Air Ministry in conjunction with the local Educational Authorities throughout the country.

Candidates must be physically fit and be between 15 and 16½ at the time of entry, although in the case of the Air Ministry examination the upper age limit is, under certain conditions, extended to 17 years.

The syllabus, which is the same in both examinations, consists of mathematics, experimental science, English, and a general paper, and has been designed to be suitable for boys still at school and following a normal course of instruction.

The closing date for entries for the Civil Service examination is August 30. This examination will be conducted by the Commissioners at the following centres:—London, Birmingham, Belfast, Chatham, Edinburgh, Plymouth, and Portsmouth. Applications to sit at this examination should be made at once to the Secretary, Civil Service Commission, Burlington Gardens, London, W.1. The entry fee is 5s.

The Air Ministry examination is confined to boys nominated by the local Education Authorities of the country and by the governing bodies of certain approved schools and associations. The closing date for entry is October 2. For this examination there is no entry fee.

Boys who are still at school, who wish to compete in the Air Ministry examination, should make application to their headmasters with a view to securing a nomination from the Education Authorities responsible for the school. In the case of boys who have left school, application may be made to the Advisory Committee for Juvenile Employment in the area, while boy scouts can apply to the authorities of the Boy Scout Association, and Territorial Cadets to the officer commanding their unit.

When appointed as aircraft apprentices, boys are given three years' training in a skilled trade and general education by civilian schoolmasters during this period up to the standard of a good technical school. The principal trades open to boys, who are invited in advance to indicate their preference, are carpenter-rigger, fitter, copper-smith, wireless operator mechanic, electrician, instrument maker and draughtsman. In assigning boys to the various trades, every endeavour is made to give effect to each boy's individual preference, the wishes of the boys in this respect being considered

in the order of their position on the examination list.

During the period of training there is careful supervision of health and general welfare, medical attendance, religious instruction from the chaplains of several denominations, and recreation facilities. Six weeks' annual leave is granted.

Pay is given, under existing regulations, at 1s. 6d. a day until the age of 18, and then at 3s. a day until the course is completed.

At the end of the course the aircraft apprentice must sit a passing-out examination for promotion to the rank of leading air craftsman with pay varying from 5s. 2d. to 5s. 6d. per day. The above rates may be subject to revision in the immediate future. Those boys who do not qualify for the highest grade will be appointed as air craftsmen with slightly lower commencing rates of pay.

A certain number of the leading apprentices are sent on completion of their course to the Royal Air Force Cadet College, for training as commissioned officers. Others are given an advanced course, and are eventually appointed as N.C.O.s with the rank of corporal. There is also a reasonable chance of selection for a further number to qualify later in flying to become airmen pilots, and generally there is an opportunity for promotion to the senior N.C.O. and warrant officer ranks, and later to commissioned rank.

Headmasters and others interested in the scheme can obtain copies of the regulations for entry (A.P.134), on application to the Secretary, Air Ministry, Kingsway, W.C.2.

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## INSULIN AND DIABETES.

The subject of diabetes and its cure was discussed at the British Medical Association on July 25th, at Portsmouth.

Sir Thomas Horder presided over the "Medicine" Section, and in opening a discussion on diabetes said that the fact which led them to choose diabetes for their first debate was, of course, the introduction of insulin as a remedy for the disease. If they did not discuss insulin at that meeting of the association their patients would be much surprised, and with good reason. They would probably assume, again with reason, that in insulin the profession had a "cure" for diabetes, and that nothing more need be said on the matter. Sir Thomas Horder continued:—

"I am afraid a good many persons have already assumed this, and perhaps such an assumption is not surprising in view of certain generalisations that have got abroad, and which, if they do not carry the hallmark of authority, at least have not been authoritatively contradicted." It might be, the speaker added, "that the successful preparation of this internal secretion (insulin) of the pancreas would prove to be as great an asset to medical science by assisting the interpretation of phenomena hitherto obscure as in the provision of a therapeutic agent in diabetes. Only a superficial hearer would read into that remark a detraction from the great value of Dr. Banting's discovery. In reality such remarks enhanced its value. Had not the essence of the problem of diabetes hitherto been the almost certain fact that under that name we had been dealing not with one biochemical disturbance only, but with several? It seemed probable that the use of insulin, controlled by careful observations, would not only still further establish that fact, but would also help to mark off, much more clearly than before, certain very different types of cases of diabetes met with in practice." Sir Thomas Horder then said:—

"One result of this segregation we are already observing: certain cases of diabetes are benefited much less by insulin than are others, and this is so even when we make due allowance for all those collateral points in the dietetic part of the treatment, attention to which we know to be so important. Certain cases will doubtless be found not to be benefited at all. And if we do not make this position quite clear we shall see many patients suffer the bitter nemesis of disappointment after entertaining a false hope for which we may, quite unwittingly, have been partly responsible."

There were a number of questions which must be discussed. Sir Thomas enunciated them in detail, and thereafter called on Dr. Banting, to whom he extended a hearty welcome.

Dr. F. G. Banting, of Toronto, the discoverer of insulin, said that it would be several years before the limits of the effectiveness of insulin were known. As to patients giving themselves insulin, he quoted the case of the American commercial traveller who carried his own insulin and syringe, and described the daily application of it as being no more difficult than the morning shave. After a warning against

this practice, Dr. Banting described the experiments which led to the discovery of insulin by observing that a dog became diabetic after its pancreas had been excised. It was then found that if they ligatured the duct coming from the pancreas to the intestines they would necessarily prevent the passage of any "external" secretion. Nevertheless, though this procedure caused the pancreas to become atrophied the dog did not become diabetic. Evidently, therefore, there was an "internal" secretion which went straight into the blood stream. The structure of the pancreas was submitted to examination, and it was found to consist of two parts, namely, the main gland and some small islands of cells. The "internal" secretion, which was the active principle, "insulin," came from these cells. Further experiments were still being made. He pointed out that the discovery of insulin threw no light on the causes of diabetes.

#### DEATH OF EDWARD KNOWLES MUSPRATT.

Liverpool has lost a notable scientist and business man by the death, on the 1st inst., of the above. He was born at Linaere, near Bootle, on November 6, 1833. He was sent to a school at Worksop, conducted on Pestalozzi's principles, where much attention was paid to science and modern languages. In the holidays he saw a good deal of his father's friends, who included Dickens, Lover, Sheridan Knowles, the dramatist (who was the boy's godfather), Jerrold, Lemon, Forster, and Charlotte Cushman, the actress, and her sister Susan, who married Muspratt's brother.

In 1850 he was sent to study at Giessen, the university of the great chemist, Justus von Liebig, who became an intimate friend of the family. After a year's preparation he was admitted to the senior laboratory, and mixed with men doing original research. Liebig urged him to specialise in physiological chemistry, and when he accepted a chair at Munich, Muspratt went with him.

In the 'sixties Weldon's process for the recovery of manganese and Ludwig Mond's process for the extraction of sulphur from alkali waste were introduced in the Muspratt works. In 1890 the businesses of James Muspratt and Sons and Muspratt and Huntley were incorporated with others in the United Alkali Company, of which Muspratt was vice-chairman at his death.

ELECTRICALLY DEFLAGRATED  
MERCURY FILAMENT AS A FLASH  
LIGHT FOR INSTANTANEOUS  
PHOTOGRAPHY.

By KYOJI SUYEHIRO.

(*Jap. J. Phys.*, I. (1922), 97-100, with 1 fig. and 2 pl.)

Even for technical researches the necessity of taking an instantaneous photograph of very short exposure is not very seldom experienced. For obvious reasons, however, the use of a high tension spark is not convenient in a workshop or in a similar place. The author found that a flash light of very short duration could be obtained by exploding a mercury filament sealed in a glass capillary tube by means of an electric current passed through it. The applied voltage may be 100 volts or so. When the filament is under 0.2 mm. in diameter and the wall of capillary tube is very thin, the duration of the flash light may be shortened even to a hundred thousandth of a second. It was found that this flash light is given out from the mercury arc lit up for a short interval just after the explosion of the capillary tube.

Apart from the advantage of this method over the high tension spark with regard to its simplicity and safety, the merit of it lies in the fact that this may be used under water without any complication of arrangement.

NOTICES OF BOOKS.

*Materie, Elektrizität Energie*, von DR. WALTHER GERLACH. Pp. 195. Dresden and Leipzig: Verlag von Theodor Steinkopff. 1923. Price 3s. 3d.

Prof. Gerlach's volume on Matter, Electricity and Energy forms one of the series of monographs on Natural Science, issued under the direction of Prof. Liesegang.

The author has undertaken the task of summarising the advances and developments in Atomic Science from the enormous volume of work which has been done during the last ten years. A good account is given of recent work on Isotopy; the elucidation of the structure of the Atom and the Atomic Nucleus; the changing of the physical state of the Atom; the application of Line and X-ray spectra; analysis with the aid of X-rays; the physical basis of Photo-

chemistry, etc. Prominence is also given to the author's own experimental contributions.

That the volume contains some of the most recent developments will be gathered from the inclusion of an account of the identification of the occurrence of Hafnium in Zirconium minerals by Coster and Hevesy. This has, however, been taken from German sources (*Naturwissenschaften*, 1923, Vol. VIII). It is indeed noticeable that much recent English and American research work has evidently escaped the author's attention. This is undoubtedly due to the prohibitive cost of English books and periodicals in Germany and most other European countries. Whilst the present unsettled state of affairs lasts, English publishers cannot hope for any Continental demand, and the dissemination of scientific knowledge will remain retarded.

As it is, foreign scientific publications are almost inaccessible to German scientists, who are obliged to rely upon the meagre abstracts in their *Centralblätter* for such information. The correctness of this is well illustrated by a perusal of the volume under review.

Prof. Gerlach's book summarises much recent work on the ultimate structure of matter, and should prove of value to chemists, physicists, and others interested in this subject.

We have received from Messrs. Robt. Boyle & Sons a booklet dealing with the ventilation of public buildings.\*

The authors have devoted themselves to the study of ventilation on truly scientific lines, and have had a world-wide practical experience in the subject.

The book in question deals exhaustively with the practical application of ventilation, and it contains a fund of information as to the methods of ventilation adopted for the Houses of Parliament, the Guildhall, and other public buildings. The relative merits of natural and artificial ventilation are fully discussed, and the opinions of many eminent authorities are quoted.

The book will be found of great use not

\* *The Ventilation of Public Buildings*, by ROBERT BOYLE. Robert Boyle & Sons, London. Price 6s. net.

only to architects and builders, but to those responsible for public buildings generally, as it explains very clearly the principles involved in a successful system of ventilation, and also explains many of the failures that are unhappily often apparent in some of our important public buildings.

The work is well illustrated with drawings and diagrams that help greatly in understanding the theories advanced.



THIS list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 20718—Canadian Electro Products Co., Ltd.—Manufacture of acetaldehyde. Aug. 15.  
 21022—Christenson, O. L.—Producing ammonium chloride from ammoniacal hot distillation or generator gases. Aug. 18.  
 20949—Neuss, O.—Manufacture of products from urea and formic aldehyde. Aug. 17.  
 21006—Pintsch Akt-Ges.—Process for obtaining nitric oxide. Aug. 18.

#### Specifications Published this Week.

- 201624—Galbraith, W. L., and Leacock, W., and Tallantyre, S. B. Manufacture of condensation products from carbazole and p-nitrosophenol and its derivatives.  
 190448—Leggo, A. V.—Furnaces or the like for ore-roasting or like operations.

#### Abstract Published this Week.

- 199886—Catalytic oxidation of organic compounds.—Badische Anilin & Soda Fabrik, Ludwigshafen-on-Rhine, Germany.

*Aldehydes; ketones; catalytic agents, preparation of.*—The partial oxidation of organic compounds is effected by passing the compound in the gaseous or vapour phase, in admixture with an oxygen-containing gas, over boric or phosphoric acid or their salts. The catalytic materials are preferably mounted on a carrier; thus clay, fire-brick or magnesia is soaked with boric or phosphoric acid, or silica, kieselguhr, a metallic oxide, carbonate or nitrate is introduced into molten boric acid. Mixed catalysts, obtained by adding boric or phosphoric acid to molten metal salts such as nitrates, may be used. According to the examples, (1) formaldehyde is produced by passing ethylene and oxygen over boric or phosphoric acid or their salts mounted on burnt clay or diatomaceous earth; the gases may circulate over the contact mass, the formaldehyde being absorbed in water and further ethylene and oxygen being introduced continuously or at intervals; methane, acetone, ethyl alcohol and cyclohexanone may also be oxidised to formaldehyde in a similar way; (2) anthracene and air passed over the catalytic material yield anthraquinone, benzyl alcohol gives benzaldehyde, and ethyl alcohol produces acetaldehyde.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

### CITY OF CARDIFF EDUCATION COMMITTEE.

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#### DEPARTMENT OF INDUSTRIAL CHEMISTRY.

Head of Department —

H. W. WEBB, M.Sc., F.I.C.  
 Session 1923-24.

(Commencing on Tuesday, 2nd October, 1923).

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JOHN J. JACKSON,  
 Director of Education,  
 CITY HALL, CARDIFF.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3309.

[BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE: LIVERPOOL, 1923.]

## THE PRESIDENTIAL ADDRESS. THE ELECTRICAL STRUCTURE OF MATTER.

BY PROFESSOR SIR ERNEST RUTHERFORD,  
D.Sc., LL.D., PH.D., F.R.S.,

*President of the Association.*

It was in 1896 that this Association last met in Liverpool, under the presidency of the late Lord Lister, that great pioneer in antiseptic surgery, whose memory is held in affectionate remembrance by all nations. His address, which dealt mainly with the history of the application of antiseptic methods to surgery and its connection with the work of Pasteur, that prince of experimenters, whose birth has been so fittingly celebrated this year, gave us in a sense a completed page of brilliant scientific history. At the same time, in his opening remarks, Lister emphasised the importance of the discovery by Röntgen of a new type of radiation, the X-rays, which we now see marked the beginning of a new and fruitful era in another branch of science.

The visit to your city in 1903 was for me a memorable occasion, for it was here that I first attended a meeting of this Association, and here that I read my first scientific paper. But of much more importance, it was here that I benefited by the opportunity, which these gatherings so amply afford, of meeting for the first time many of the distinguished scientific men of this country and the foreign representatives of science who were the guests of this city on that occasion. The year 1896 has always seemed to me a memorable one for other reasons, for on looking back with some sense of perspective we cannot fail to recognise that the last Liverpool meeting marked the beginning of what has been aptly termed the heroic age of Physical Science. Never before in the history of physics has there been witnessed such a period of intense activity when discoveries of fundamental importance have followed one another with such bewildering rapidity.

The discovery of X-rays by Röntgen had been published to the world in 1895, while

the discovery of the radioactivity of uranium by Becquerel was announced early in 1896. Even the most imaginative of our scientific men could never have dreamed at that time of the extension of our knowledge of the structure of matter that was to develop from these two fundamental discoveries, but in the records of the Liverpool meeting we see the dawning recognition of the possible consequences of the discovery of X-rays, not only in their application to medicine and surgery, but as a new and powerful agent for attacking some of the fundamental problems of physics. The address of Professor J. J. Thomson, President of Section A, was devoted mainly to a discussion of the nature of the X-rays, and the remarkable properties induced in gases by the passage of X-rays through them—the beginning of a new and fruitful branch of study.

In applied physics, too, this year marked the beginning of another advance. In the discussion of a paper which I had the honour to read, on a new magnetic detector of electrical waves, the late Sir William Preece told the meeting of the successful transmission of signals for a few hundred yards by electric waves which had been given by Sir Oliver Lodge at the Oxford Meeting of this Association in 1894. It is startling to recall the rapidity of the development from such small beginnings of the new method of wireless intercommunication over the greatest terrestrial distances. In the last few years this has been followed by the even more rapid growth of the allied subject of radiotelephony as a practical means of broadcasting speech and music to distances only limited by the power of the transmitting station. The rapidity of these technical advances is an illustration of the close interconnection that must exist between pure and applied science if rapid and sure progress is to be made. The electrical engineer has been able to base his technical developments on the solid foundation of Maxwell's electromagnetic theory and its complete verification by the researches of Hertz, and also by the experiments of Sir Oliver Lodge in this University—a verification which was completed long before the practical possibilities of this new method of signalling had been generally recognised. The later advances in radiotelegraphy and radiotelephony have largely depended on the application of the results of fundamental researches on the properties of electrons, as illustrated in the

use of the thermionic valve or electron tube which has proved such an invaluable agent both for the transmission and reception of electric waves.

It is of great interest to note that the benefits of this union of pure and applied research have not been one-sided. If the fundamental researches of the workers in pure science supply the foundations on which the applications are surely built, the successful practical application in turn quickens and extends the interest of the investigator in the fundamental problem, while the development of new methods and appliances required for technical purposes often provides the investigator with means of attacking still more difficult questions. This important reaction between pure and applied science can be illustrated in many branches of knowledge. It is particularly manifest in the industrial development of X-ray radiography for therapeutic and industrial purposes, where the development on a large scale of special X-ray tubes and improved methods of excitation has given the physicist much more efficient tools to carry out his researches on the nature of the rays themselves and on the structure of the atom. In this age no one can draw any sharp line of distinction between the importance of so-called pure and applied research. Both are equally essential to progress, and we cannot but recognise that without flourishing schools of research on fundamental matters in our universities and scientific institutions technical research must tend to wither. Fortunately there is little need to labour this point at the moment, for the importance of a training in pure research has been generally recognised. The Department of Scientific and Industrial Research has made a generous provision of grants to train qualified young men of promise in research methods in our scientific institutions, and has aided special fundamental researches which are clearly beyond the capacity of a laboratory to finance from its own funds. Those who have the responsibility of administering the grants in aid of research both for pure and applied science will need all their wisdom and experience to make a wise allocation of funds to secure the maximum of results for the minimum of expenditure. It is fatally easy to spend much money in a direct frontal attack on some technical problem of importance when the solution may depend on some addition to knowledge which can be gained in some other field of scientific inquiry possibly at

a trifling cost. It is not in any sense my purpose to criticise those bodies which administer funds for fostering pure and applied research, but to emphasise how difficult it is to strike the correct balance between the expenditure on pure and applied science in order to achieve the best results in the long run.

It is my intention this evening to refer very briefly to some of the main features of that great advance in knowledge of the nature of electricity and matter which is one of the salient features of the interval since the last meeting of this Association in Liverpool.

In order to view the extensive territory which has been conquered by science in this interval, it is desirable to give a brief summary of the state of knowledge of the constitution of matter at the beginning of this epoch. Ever since its announcement by Dalton the atomic theory has steadily gained ground, and formed the philosophic basis for the explanation of the facts of chemical combination. In the early stages of its application to physics and chemistry it was unnecessary to have any detailed knowledge of the dimensions or structure of the atom. It was only necessary to assume that the atoms acted as individual units, and to know the relative masses of the atoms of the different elements. In the next stage, for example, in the kinetic theory of gases, it was possible to explain the main properties of gases by supposing that the atoms of the gas acted as minute perfectly elastic spheres. During this period, by the application of a variety of methods, many of which were due to Lord Kelvin, rough estimates had been obtained of the absolute dimensions and mass of the atoms. These brought out the minute size and mass of the atom and the enormous number of atoms necessary to produce a detectable effect in any kind of measurement. From this arose the general idea that the atomic theory must of necessity for ever remain unverifiable by direct experiment, and for this reason it was suggested by one school of thought that the atomic theory should be banished from the teaching of chemistry, and that the law of multiple proportions should be accepted as the ultimate fact of Chemistry.

While the vaguest ideas were held as to the possible structure of atoms, there was a general belief among the more philosophically minded that the atoms of the elements could not be regarded as simple un-

connected units. The periodic variations of the properties of the elements brought out by Mendeléef were only explicable if atoms were similar structures in some way constructed of similar material. We shall see that the problem of the constitution of atoms is intimately connected with our conception of the nature of electricity. The wonderful success of the electromagnetic theory had concentrated attention on the medium or ether surrounding the conductor of electricity, and little attention had been paid to the actual carriers of the electric current itself. At the same time the idea was generally gaining ground that an explanation of the results of Faraday's experiments on electrolysis was only possible on the assumption that electricity, like matter, was atomic in nature. The name "electron" had even been given to this fundamental unit by Johnstone Stonev, and its magnitude roughly estimated, but the full recognition of the significance and importance of this conception belongs to the new epoch.

For the clarifying of these somewhat vague ideas, the proof in 1897 of the independent existence of the electron as a mobile electrified unit, of mass minute compared with that of the lightest atom, was of extraordinary importance. It was soon seen that the electron must be of a constituent of all the atoms of matter, and that optical spectra had their origin in their vibrations. The discovery of the electron and the proof of its liberation by a variety of methods from all the atoms of matter was of the utmost significance, for it strengthened the view that the electron was probably the common unit in the structure of atoms which the periodic variation of the chemical properties had indicated. It gave for the first time some hope of the success of an attack on that most fundamental of all problems—the detailed structure of the atom. In the early development of this subject science owes much to the work of Sir J. J. Thomson, both for the boldness of his ideas and for his ingenuity in developing methods for estimating the number of electrons in the atom, and of probing its structure. He early took the view that the atom must be an electrical structure, held together by electrical forces, and showed in a general way lines of possible explanation of the variation of physical and chemical properties of the elements, exemplified in the periodic law.

In the meantime our whole conception of the atom and of the magnitude of the

forces which held it together were revolutionised by the study of radioactivity. The discovery of radium was a great step in advance, for it provided the experimenter with powerful sources of radiation specially suitable for examining the nature of the characteristic radiations which are emitted by the radioactive bodies in general. It was soon shown that the atoms of radioactive matter were undergoing spontaneous transformation, and that the characteristic radiations emitted, viz., the  $\alpha$ ,  $\beta$ , and  $\gamma$  rays, were an accompaniment and consequence of these atomic explosions. The wonderful succession of changes that occur in uranium, more than thirty in number, was soon disclosed and simply interpreted on the transformation theory. The radioactive elements provide us for the first time with a glimpse into Nature's laboratory, and allow us to watch and study but not control the changes that have their origin in the heart of the radioactive atoms. These atomic explosions involve energies which are gigantic compared with those involved in any ordinary physical or chemical process. In the majority of cases an  $\alpha$  particle is expelled at high speed, but in others a swift electron is ejected often accompanied by a  $\gamma$  ray, which is a very penetrating X-ray of high frequency. The proof that the  $\alpha$  particle is a charged helium atom for the first time disclosed the importance of helium as one of the units in the structure of the radioactive atoms, and probably also in that of the atoms of most of the ordinary elements. Not only then have the radioactive elements had the greatest direct influence on natural philosophy, but in subsidiary ways they have provided us with experimental methods of almost equal importance. The use of  $\alpha$  particles as projectiles with which to explore the interior of the atom has definitely exhibited its nuclear structure, has led to artificial disintegration of certain light atoms, and promises to yield more information yet as to the actual structure of the nucleus itself.

The influence of radioactivity has also extended to yet another field of study of fascinating interest. We have seen that the first rough estimates of the size and mass of the atom gave little hope that we could detect the effect of a single atom. The discovery that the radioactive bodies expel actual charged atoms of helium with enormous energy altered this aspect of the problem. The energy associated with a single  $\alpha$  particle is so great that it can read-

ily be detected by a variety of methods. Each  $\alpha$  particle, as Sir Wm. Crookes first showed, produces a flash of light easily visible in a dark room when it falls on a screen coated with crystals of zinc sulphide. This scintillation method of counting individual particles has proved invaluable in many researches, for it gives us a method of unequalled delicacy for studying the effects of single atoms. The  $\alpha$  particle can also be detected electrically or photographically, but the most powerful and beautiful of all methods is that perfected by Mr. C. T. R. Wilson for observing the track through a gas not only of an  $\alpha$  particle but of any type of penetrating radiation which produces ions or of electrified particles along its path. The method is comparatively simple, depending on the fact, first discovered by him, that if a gas saturated with moisture is suddenly cooled each of the ions produced by the radiation becomes the nucleus of a visible drop of water. The water-drops along the track of the  $\alpha$  particle are clearly visible to the eye, and can be recorded photographically. These beautiful photographs of the effect produced by single atoms or single electrons appeal, I think, greatly to all scientific men. They not only afford convincing evidence of the discrete nature of these particles, but give us new courage and confidence that the scientific methods of experiment and deduction are to be relied upon in this field of inquiry; for many of the essential points brought out so clearly and concretely in these photographs were correctly deduced long before such confirmatory photographs were available. At the same time, a minute study of the detail disclosed in these photographs gives us most valuable information and new clues on many recondite effects produced by the passage through matter of these flying projectiles and penetrating radiations.

In the meantime a number of new methods had been devised to fix with some accuracy the mass of the individual atom and the number in any given quantity of matter. The concordant results obtained by widely different physical principles gave great confidence in the correctness of the atomic idea of matter. The method found capable of most accuracy depends on the definite proof of the atomic nature of electricity and the exact valuation of this fundamental unit of charge. We have seen that it was early surmised that electricity

was atomic in nature. This view was confirmed and extended by a study of the charges carried by electrons,  $\alpha$  particles, and the ions produced in gases by X-rays and the rays from radioactive matter. It was first shown by Townsend that the positive or negative charge carried by an ion in gases was invariably equal to the charge carried by the hydrogen ion in the electrolysis of water, which we have seen was assumed, and assumed correctly, by Johnstone Stoney to be the fundamental unit of charge. Various methods were devised to measure the magnitude of this fundamental unit; the best known and most accurate is Millikan's, which depends on comparing the pull of an electric field on a charged droplet of oil or mercury with the weight of the drop. His experiments gave a most convincing proof of the correctness of the electronic theory, and gave a measure of this unit, the most fundamental of all physical units, with an accuracy of about one in a thousand. Knowing this value, we can by the aid of electrochemical data easily deduce the mass of the individual atoms and the number of molecules in a cubic centimetre of any gas with an accuracy of possibly one in a thousand, but certainly better than one in a hundred. When we consider the minuteness of the unit of electricity and of the mass of the atom this experimental achievement is one of the most notable even in an era of great advances.

The idea of the atomic nature of electricity is very closely connected with the attack on the problem of the structure of the atom. If the atom is an electrical structure it can only contain an integral number of charged units, and, since it is ordinarily neutral, the number of units of positive charge must equal the number of negative. One of the main difficulties in this problem has been the uncertainty as to the relative part played by positive and negative electricity in the structure of the atom. We know that the electron has a negative charge of one fundamental unit, while the charged hydrogen atom, whether in electrolysis or in the electric discharge, has a charge of one positive unit. But the mass of the electron is only  $1/1840$  of the mass of the hydrogen atom, and though an extensive search has been made, not the slightest evidence has been found of the existence of a positive electron of small mass like the negative. In no case has a positive charge been found associated with a mass less than that of the charged atom of hydrogen. This difference between positive and negative

electricity is at first sight very surprising, but the deeper we pursue our inquiries the more this fundamental difference between the units of positive and negative electricity is emphasised. In fact, as we shall see later, the atoms are quite unsymmetrical structures with regard to the positive and negative units contained in them, and indeed it seems certain that if there were not this difference in mass between the two units, matter, as we know it, could not exist.

It is natural to inquire what explanation can be given of this striking difference in mass of the two units. I think all scientific men are convinced that the small mass of the negative electron is to be entirely associated with the energy of its electrical structure, so that the electron may be regarded as a disembodied atom of negative electricity. We know that an electron in motion, in addition to possessing an electric field, also generates a magnetic field around it, and energy in the electromagnetic form is stored in the medium and moves with it. This gives the electron an apparent or electrical mass, which, while nearly constant for slow speeds, increases rapidly as its velocity approaches that of light. This increase of mass is in good accord with calculation, whether based on the ordinary electrical theory or on the theory of relativity. Now we know that the hydrogen atom is the lightest of all atoms, and is presumably the simplest in structure, and that the charged hydrogen atom, which we shall see is to be regarded as the hydrogen nucleus, carries a unit positive charge. It is thus natural to suppose that the hydrogen nucleus is the atom of positive electricity, or positive electron, analogous to the negative electron, but differing from it in mass. Electrical theory shows that the mass of a given charge of electricity increases with the concentration, and the greater mass of the hydrogen nucleus would be accounted for if its size were much smaller than that of the electron. Such a conclusion is supported by evidence obtained from the study of the close collisions of  $\alpha$  particles with hydrogen nuclei. It is found that the hydrogen nucleus must be of minute size, of radius less than the electron, which is usually supposed to be about  $10^{-13}$  cms.; also the experimental evidence is not inconsistent with the view that the hydrogen nucleus may actually be much smaller than the electron. While the greater mass of the posi-

tive atom of electricity may be explained in this way, we are still left with the enigma why the two units of electricity should differ so markedly in this respect. In the present state of our knowledge it does not seem possible to push this inquiry further, or to discuss the problem of the relation of these two units.

We shall see that there is the strongest evidence that the atoms of matter are built up to these two electrical units, viz., the electron and the hydrogen nucleus or proton, as it is usually called when it forms part of the structure of any atom. It is probable that these two are the fundamental and indivisible units which build up our universe, but we may reserve in our mind the possibility that further inquiry may some day show that these units are complex, and divisible into even more fundamental entities. On the views we have outlined the mass of the atom is the sum of the electrical masses of the individual charged units composing its structure, and there is no need to assume that any other kind of mass exists. At the same time, it is to be borne in mind that the actual mass of an atom may be somewhat less than the sum of the masses of component positive and negative electrons when in the free state. On account of the very close proximity of the charged units in the nucleus of an atom, and the consequent disturbance of the electric and magnetic field surrounding them, such a decrease of mass is to be anticipated on general theoretical grounds.

(To be continued.)

## THE QUANTUM THEORY.

BY R. F. HUNTER, F.C.S.

(Continued from Page 147.)

When  $\frac{V}{\beta_0 v} > 0.9$

the term 
$$\frac{e\beta_0 v^2 \left(\frac{\beta_0 v}{T}\right)^2}{(e\beta_0 v/T-1)}$$

approximates to the value 1, and hence our older expression is merely a first approximation, viz.:

$$Cv = 3R.$$

Unfortunately, Einstein's expression was shown to hold only in a quantitative manner, and further correction was necessary. This was undertaken by Debye.

The fallacy in Einstein's investigation lay in this way: Einstein assumed for the sake of simplicity that a vibrating particle only gives rise to monochromatic light and absorbs such; Debye, observing this, worked out an expression for atomic heat on the basis of absorption and emission of a number of vibration frequencies covering, as a matter of fact, the whole spectrum. He assumed firstly, that a vibrating atom in a solid cannot vibrate simply in S.H.M. with one frequency, but owing to the effect of other neighbouring atoms and the probability of collision, assumes a complex mode of vibration; the complex vibration being calculated by the method of Fourier. If the temperature,  $T$ , be a multiple of a

characteristic constant  $\frac{T}{\theta}$  for a substance,

Atomic heat is a universal function of  $\frac{T}{\theta}$

Further, at low temperature, Debye deduced that the atomic heat of solids  $\propto T^3$ .

Hence the atomic heat would be  $\propto T^4$ .

Debye's expression for the energy,  $U$ , of a solid vol.  $V$  containing  $N$  atoms is of the form

$$U = 9N \int_0^{V_m} \frac{h\nu}{e^{h\nu/kT} - 1} \nu^2 d\nu \quad (1)$$

Further, giving the constant  $\theta$ , the meaning

$$\theta = \frac{h\nu_m}{k} = \beta\nu_m \quad (2)$$

and introducing into (1) a new variable,

without dimensions,  $\xi = \frac{h\nu}{kT}$

one arrives at:

$$U = 9NkT \left( \frac{kT}{h\nu_m} \right)^3 \int_0^{\frac{h\nu_m/kT}{\xi}} \frac{\xi^3 d\xi}{e^\xi - 1} \quad (3)$$

Substituting, one obtains:

$$U = 9NkT \left( \frac{T}{\theta} \right)^3 \int_0^{\frac{\theta T}{\xi}} \frac{\xi^3 d\xi}{e^\xi - 1} \quad (4)$$

Differentiating, one obtains:

$$C_v = 3Nk \left( \frac{12}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{3x}{e^x - 1} \right) \quad (5)$$

which is Debye's equation.

Debye's formula subjected to experimental tests proved to agree exceedingly well with experimental results.

Two theories which deserve mention before we pass on to the Rutherford Bohr theory, are the theories of Bjerrum and of Kruger.

The Bjerrum theory has been of considerable use in the question of the rotational spectrum of water vapour constructed by Eucken.

Kruger's theory can be regarded as a modification of the Rutherford Bohr theory or, to be more accurate, an application of it.

Kruger accepts Rutherford's theory of atoms, and regards gaseous molecules as gyroscopic in nature, meaning that molecular rotation is regarded as impossible, and molecules are only capable of carrying out precessional vibrations. These vibrations are regarded as being fundamentally different from the ordinary vibrations of atoms along the line forming their centres.

Considering molecular collision, Kruger postulates that the ring of rotating electrons of a Bohr atom, which serve to hold two atoms in union, suffers displacement in a direction perpendicular to the direction of motion, with the ultimate result that the atoms themselves describe small circular or approximately circular orbits and thus the molecule as one whole exhibits a precessional kind of motion.

Further, Kruger points out that such motion is wholly kinetic in nature, and involves two degrees of freedom. Now in the range of temperature in which the principle of equipartition is known to hold good, the energy term will be one corresponding to two degrees of freedom, and one degree =

$$\frac{1}{2} RT; \text{ therefore the energy is } R.T. \text{ which}$$

is identical with the energy which Bjerrum postulated for diatomic molecules on the basis of molecular rotation as a whole over the same temperature region.

Kruger's theory possesses the advantage that it furnishes an explanation of the behaviour of monoatomic gases, viz., the behaviour of inert gases such as argon.

We now come to one of the most important pieces of work on the quantum theory, namely, Bohr's application of the quantum theory to the Rutherford Atom Model: and it seems necessary to give first a vague outline of the Rutherford Bohr theory of the atom.

Briefly the theory can be described as follows: We consider the atom as consisting of a nuclear charge surrounded by a series of electrons rotating in definite orbits, nearly the whole mass being ascribed to the nucleus. The nucleus is very small in itself as compared with the whole volume of the atom. The outer row of electrons are those which gave the atom its characteristic chemical properties, such as valency, etc. The electrons on Rutherford's atom are regarded as "atmosphere" electrons. The above is a rough postulation of the Rutherford atom as conceived by its inventor in 1911.

Bohr pointed out that the above atom suffered from the drawback of a system of "atmosphere" electrons, a system unstable from the point of view of classical electrodynamics, but if Planck's conception was introduced the trouble vanished, instability no longer would exist from the theoretical point of view.

Rutherford considered the hydrogen atom as follows: as consisting of a nucleus with a single electron describing a closed orbit around it. Bohr considers while the electron is in a steady state of rotating motion in the aforesaid orbit, it is neither radiating nor absorbing energy. Radiation he considers to be the result of electron transference from one orbit to another. The quantum theory assumes that during the passage of the electron from one stable orbit to another homogeneous radiation is given out or absorbed at a definite frequency, and the amount given out or absorbed is  $h\nu$  where  $h$  is Planck's constant.

The equations deduced from this are familiar ones, viz.:

$$W = \frac{2\pi mc^2 E^2}{\tau^2 h^2} \quad (1)$$

$$W = \frac{4\pi^2 mc^2 E^2}{\tau^3 h^3} \quad (2)$$

$$2a = \frac{\tau^2 h^2}{2\pi^2 mcE} \quad (3)$$

where  $W$  is energy transference during change;

$e$  is charge on the electron;

$E$  is charge on the nucleus;

$W$  is angular velocity;

$2a$  major axes of orbit.

Finally one arrives at the expression:

$$v = \frac{2\pi mc^4}{h^3} \begin{pmatrix} \mathbf{J} & - & \mathbf{J} \\ \tau_2^2 & & \tau_1^2 \end{pmatrix}$$

which gives the frequency of the homogeneous radiation emitted by a gas when the atomic system changes from a stationary state defined by  $\tau_1$  to one  $\tau_2$ .

By taking the expression and putting  $\tau_2 = 2$  and allowing  $\tau_1$  to vary, we get the Balmer series of lines of hydrogen spectrum. This is the most definite proof of the Bohr theory, and has therefore an effect on the corresponding quantum theory.

We have two more matters to consider briefly with regard to the quantum hypothesis, and they are: the photo electric effect and the Nernst heat theorem, in their relation to the quantum hypothesis: these we shall deal briefly with in the respective order: Photo-electric effect and Quantum Theory; Nernst Heat Theorem and Quantum Theory.

Some forty years ago what we call the "photo electric effect" was obtained by Hallwachs, who showed a charged body exposed to ultra violet light loses its charge. In the photo-electric effect we apparently deal with two phenomena: firstly, the normal photo-electric effect, and secondly the selective photo-electric effect. The effect produced moving electrons set free at surface depends on, firstly, the number of electrons emitted in unit time, and secondly on the speed of these electrons.

One of the most striking parts of the photo-electric effect is that the speed of electrons is the same for a given frequency of light independent of the intensity of the light, and more than this, on keeping the intensity constant and varying the quality of the light the speed of the electrons increases as the frequency increases. These facts have found an explanation on the quantum theory, in which, as we have seen, we regard light as heterogeneous. Sir J. J. Thomson enunciated the view we hold of the problem roughly as follows: Radiant energy which travels out from a source with a wave is not spread uniformly over the wave front, but is concentrated on those parts of the front where the pulses travel

along the lines of force. The energy of the wave, therefore, tends to become collected into regions, these regions being portions of lines of force occupied by pulses. The distribution of energy appears to be analogous almost to the old emission theory, the energy being located on moving particles sparsely distributed throughout space. The energy appearing in bundles and the energy content of such bundles being constant during travelling along lines of force. Thus when light falls on a metal plate, if the distance of the source is increased, we diminish the number of bundles falling on given area, but the energy in individual units will not be diminished, but any effect which is produced will be less frequent but of the same character as before. Ladenburg recently found that the velocities of corpuscles emitted under the action of ultra violet light of varied wave lengths, varies continuously with the frequency, hence the velocity is proportional to the frequency, hence although the velocity of corpuscles is independent of the intensity of the lights, it varies apparently in a continuous manner with the quality of the light; this clearly renders it impossible to consider the corpuscles as being expelled by the explosion of the molecule

Einstein gave the expression:

$$v_e = \frac{1}{2} mv^2 = hv - hv_0$$

to the quantitative relation between the theory of quantum and the photo-electric effect where  $\frac{1}{2} mv^2$  is the K.E. of an electron emitted by light of frequency,  $v$ ,  $v_0$  is the threshold frequency.

Einstein's law, which can be stated as follows, "When a photochemical reaction takes place owing to the absorption of radiation in terms of quanta, each single molecule of a photosensitive substance requiring just one quantum  $hv_0$ , in order that it may be decomposed," has been investigated by Bodenstein, who found the law to break down badly, because one quantum is apparently capable of decomposing several molecules. Baley has dealt with this problem, and his argument is essentially as follows: that in the case of a dissolved substance which reacts photochemically, less energy is required per molecule than is required for the same substance in a gaseous state, and hence Einstein's law will only hold for the gaseous state.

We now consider our last problem, namely: the relation between the Nernst Heat Theorem and the Quantum Hypothesis. The application of the quantum hypo-

thesis to the atomic heats of bodies in a solid state lead us to expect that at low temperatures, atomic heats would become nearly zero. Further, if we consider chemical reaction at low temperatures, the hypothesis of quantum lead us to the conclusion that for low temperatures the reaction between two solids will be given by:

$$\frac{dU}{dT} = 0$$

This is in agreement with the Nernst theory, which states that

$$L \lim_{T \rightarrow 0} \left( \frac{dA}{dT} \right) = 0$$

$$L \lim_{T \rightarrow 0} \left( \frac{dU}{dT} \right) = 0$$

The relation  $\frac{dA}{dT} = 0$  is in agreement

also with the Plank-Einstein hypothesis regarding energy distribution in solids, because we can say this: as molecules or atoms of a solid body at low temperature possess infinitesimally small K.E. of vibration, the mutual distance apart will only change slightly with temperature over a range of this region, and hence the mutual potential energy of the atom will be nearly constant, hence their free energy will be constant, and hence mathematically we have

$$L \lim_{T \rightarrow 0} \frac{dA}{dT} = 0.$$

In composing this article, I have followed more or less the treatment of the subject by Lewis in Vol. III. of his "System of Physical Chemistry." Space unfortunately has prevented the production of anything but the mistiest of misty outlines of the subject. Many things of importance have been no more than mentioned; many more have not even been mentioned. The mathematics I have openly shirked. The only hope which I express for the article is that it may have dispelled amongst some chemists the fear and awe which the title, "Quantum Theory," appears to have for many of us who are research organic chemists, and not mathematical physicists.



## AMERICAN DYE PRODUCTION.

## THE DEMAND FOR STANDARDISATION.

Prior to the war Germany dominated the world's dye markets, producing about three-fourths of all synthetic dyes. Of the remaining fourth about one-half were made of German intermediates, and consequently the production of these dyes was dependent upon Germany. Soon after the declaration of war the supply of German dyes was cut off from the world's markets. An acute dye famine developed, threatening the activities of the vast textile and other industries dependent upon dyes for their operation. Prices increased to previously unheard of levels, and certain dyes were not to be had at any price. During and since the war the United States, the United Kingdom and France have made extensive developments in the manufacture of dyes, and have exported dyes in significant quantities since the signing of the Armistice. The complete German monopoly of the world's dye production has been broken, at least temporarily, if not permanently. Extensive developments in dye manufacture in the various countries have resulted in an approximate doubling of the world's capacity to produce synthetic dyes, and sharp competition may be expected in the world's dye markets. It is already in evidence in the Far East.

The German dye industry, for instance, offers a united front to the world in a combination known as the I.G. (Interessen Gemeinschaft). It possesses the advantage of cumulated experience, lower manufacturing costs, and a unified organisation for buying and selling. The three Swiss dye manufacturers have also formed an amalgamation. China leads the world as a consumer of dyes with a consumption estimated at about 70 million lbs. per annum; the United States ranks second with an average consumption of about 55 million lbs., followed by the United Kingdom with a consumption of nearly 50 million lbs. per year. It is expected that Germany will make every endeavour to recover a part of her former trade with these three dye-consuming nations. In case protective measures are retained by the new dye-producing countries Germany may resort to the establishment of factories or seek affiliations, as has already been done by the Swiss manufacturers in establishing plants in both the United States and the United Kingdom.

The foregoing has been taken from an advance summary\* of the Report on the annual Census of Dyes and other Synthetic Organic Chemicals recently completed by the United States Tariff Commission. The following statement of the dye industry of the United States has been extracted from the same source:—

## GROWTH OF DYE PRODUCTION.

The Report shows that during the year 1922 the domestic dye and organic chemical industry made notable progress. Many products were manufactured for the first time in the United States, and there were large increases in the quantity of production, with conspicuous reductions in prices.

The domestic production of dyes during the year by 87 firms was 64,632,187 lb., an increase of 66 per cent. over that of 1921. The sales for 1922 totalled 69,107,105 lb., valued at 41,463,790 dols. The size of the industry in 1922 was in sharp contrast with that of 1914, when only seven firms manufactured a total of 6,619,120 lb., valued at 2,470,096 dols. The dye industry in that period was in no sense a self-contained one, as the dyes produced were made almost entirely of intermediates imported chiefly from Germany. The increase in production during 1922 was largely due to an expansion in general business. Beginning about June the textile and other dye-consuming industries became more active after the depression, and during the remainder of the year the demand for dyes steadily increased.

## LARGE PRICE REDUCTIONS.

The average selling price of all domestic dyes for 1922 was 60 cents. per lb., compared with 83 cents in 1921 and 1 dol. 26 cents per lb. in 1917. The 1922 figures represent a 28 per cent. decline from that of 1921. There were price reductions for both the bulk colours and dyes consumed in smaller quantities. The average price of indigo in 1921 was 45 cents per lb., compared with 24 cents in 1922, a 47 per cent. decrease.

## INCREASED OUTPUT OF VAT AND ALIZARIN DYES.

One of the conspicuous developments of the year was the increased production of vat and alizarin dyes. The vat colours are of great complexity and have presented serious difficulties in their commercial production. Their use is on the increase, as the public is beginning to recognise that

fast shades are obtainable on cotton goods. The alizarin dyes are of great value in wool dyeing, and the addition to this field of new dyes and the increased production of other dyes is a significant step in the development of a self-contained dye industry. The total production in 1922 of vat dyes (not including indigo) was 1,075,992 lb., compared with 345,152 lb. in 1921. The production of the anthraquinone dyes, which includes alizarin dyes and a large part of the vat dyes, was 1,234,963 lb.

#### PRODUCTION OF NEW DYES.

Many important dyes were produced for the first time on a commercial scale in 1922. These comprise colours of great value for the dyeing of either silk, cotton, or wool, such as vat dyes, alizarin, developed cotton dyes, mordant and acid dyes. The production of these dyes has resulted only after large expenditures on research and most painstaking investigations. There are, however, still gaps to be filled in certain vat dyes and some of the mordant, acid and direct dyes.

#### QUALITY AND STANDARDISATION OF AMERICAN DYES.

Dye for dye, with relatively few exceptions, domestic products are now found equal to pre-war German dyes. In the early stages of the United States dye industry, after the outbreak of the Great War, many dyes were lacking in uniformity of strength and quality. This condition, however, no longer prevails, as is attested to by the largest silk and woollen manufacturers and cotton printers and dyers.

#### RATIO OF PRODUCTION TO CONSUMPTION.

The United States produces about 93.5 per cent. of the dyes actually consumed in the country. The imports of dyes in 1922 totalled 3,982,631 lb., the production was 64,632,187 lb., and the exports totalled 6,956,593 lb. Consumption is assumed to equal production, *plus* imports, *minus* exports, or 61,658,225 lb. The imports in 1922 were 6.2 per cent. of United States production and 6.5 per cent. of consumption. In 1914 the imports were nearly 90 per cent. of consumption.

#### PRODUCTION BY CLASSES.

The production of dyes in 1922, grouped by classes according to their method of application on fibres, were as follows:—

	lb.
Acid ... ..	9,880,014
Basic dyes ... ..	2,937,585
Direct cotton dyes ... ..	11,931,737
Lake and spirit-soluble dyes ... ..	11,009,512
Mordant and chrome dyes ... ..	3,749,510
Sulphur dyes ... ..	16,913,767
Vat dyes (not including indigo) ... ..	1,075,992
Indigo ... ..	15,850,752
Unclassified dyes ... ..	1,283,127

#### DYE IMPORTS: AMOUNT AND SOURCES.

Imports of dyes into the United States last year amounted to 3,982,631 lb., valued at 5,243,258 dols., as compared with 4,252,911 lb. in 1921 and 45,950,895 lb. in 1914. Of last year's imports, 44.58 per cent. came from Germany, 43.72 per cent. from Switzerland, 5.25 per cent. from the United Kingdom, and 4.18 per cent. from Italy. The 1922 figures show a decline of dye imports from Germany, as during the previous year 48.34 per cent. and in 1920 51 per cent. came from there. Vat dyes led in quantity of imports, totalling 1,549,024 lb. (single strength); mordant and chrome dyes amounted to 716,790 lb., and direct cotton dyes to 671,621 lb.

#### EXPENDITURE ON DYE RESEARCH.

The United States coal-tar dye and chemical industry expended over 21 million dols. on research during the five years 1917-22. The accomplishments of that period and the progress of the dye industry may be attributed in no small part to the enormous expenditure on research. New dyes and other chemicals of great economic value have been developed, and the costs of production have been materially reduced.

#### DYE EXPORTS.

The export of dyes from the United States in 1922 shows a decrease in value from the previous year from 6,270,155 dols. in 1921 to 3,023,127 dols. Further, the 1922 figure is a 90 per cent. decline from that of 1920, when exports reached the maximum value of 29,823,591 dols. The large export during 1920 was due to the trade boom before German dyes made their appearance in the large dye markets of the world. The official import figures of China, India, and Japan show that large quantities of German dyes were exported to these countries after 1920, and, in addition, Swiss, French, and British dyes have been notable factors in the Far Eastern markets.

Exports of dyes for the first four months of 1923 show a recovery in value and quantity. This increased demand for American dyes, largely by the Far Eastern markets, may be attributed in part to the reduced imports of German dyes on account of the occupation of the Ruhr by the French in 1923.

#### OTHER FINISHED COAL-TAR PRODUCTS.

The total output of dyes and other finished coal-tar chemicals in the United States in 1922 by 164 firms was 88,368,131 lb., compared with 51,457,565 lb. by 147 firms in 1921, a 72 per cent. increase. Preliminary figures of the United States Geological Survey indicate that the production of coal tar and by-products from the by-product coke industry last year was the greatest in the history of the industry. The output of by-product coke was about 28½ million tons, which exceeded the production of both beehive and by-product coke during the previous year.

#### CHEMICALS OF NON-COAL TAR ORIGIN.

Conspicuous progress has also been made within the past few years in the development and manufacture of synthetic organic chemicals of non-coal tar origin. The production during 1922 was 79,202,155 lb., as compared with 21,545,186 lb. in 1921.

#### NEED FOR STANDARDISATION.

In a Memorandum\* issued by the United States Bureau of Standards on its work in connection with the standardisation of dyes it is stated that the lack of uniformity of commercial dyes in colour strength, quality and money value is well known to the trade. Before the war the dye industry was controlled by the German firms, who maintained a multiplicity of names, strengths, and qualities of dyes. The trade was accustomed, therefore, to dyestuffs of variable quality, so that when the field was opened to American manufacturers opportunity was presented for the wholesale adulteration of textile colouring matters by jobbers and brokers, whose profits entailed

a corresponding loss to legitimate industry. The demand for standardisation has come mainly from the dyers and textile manufacturers, who believe that standardisation will remedy this objectionable condition. The situation with respect to the enforcement of the standardisation features of the Tariff Act of 1922 clearly shows that there was little or no standardisation in the past, and that it is needed now.

The standardisation of dyes is in accord with modern business practice, whereby buyer and seller have a common basis of knowledge of the products of trade. Such practice leads to more economical business and better business to legitimate industry. The manufacturer of dyes, in particular, is coming to see the advantages of standardisation. In fact, standardisation may well become a distinctive feature of the American Dye Industry.

The problem of dye standardisation is first to devise methods for:—

- (1) Identification of dye species.
- (2) Determination of colour strength in terms of pure dye content or some arbitrarily chosen standard.
- (3) Determination of quality of a dye. This includes fastness tests and tests for suitability of a given product for a special use.

Then the problem is to establish standards and specifications for each dye *which will be acceptable to manufacturer and consumer.*

#### GENERAL NOTES.

##### SOUTH AFRICA—TAR OR TAR SUBSTITUTE.

His Majesty's Senior Trade Commissioner in South Africa (Mr. W. E. G. Wickham) reports a call for tenders for the supply of 1,800 tons of tar or tar substitute.

Applications for further particulars should be addressed to the Department of Overseas Trade, 35, Old Queen Street, Westminster, S.W.1.

##### MEXICO.

His Majesty's Consul-General at Mexico City (Mr. N. King) wishes to draw the attention of British traders sending catalogues to Mexico to the necessity for the payment of the recently imposed duty on such literature.

It should be noted that delivery is not permitted before this duty has been paid.

\* *The Summary of the Report of the Tariff Commission and the Memorandum of the Bureau of Standards, which have been forwarded by H.M. Representative at Washington, may be consulted by United Kingdom firms interested on application to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.*

### SODIUM ACETATE (COMMERCIAL) FOR AUSTRALIA.

Mr. S. W. B. McGregor, H.M. Senior Trade Commissioner in Australia, reports that the Victorian Railways Commissioners are calling for tenders to be presented before October 17, 1923, for the supply of fifteen tons of (commercial) sodium acetate.

Applications from United Kingdom firms for further particulars should be addressed to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1, quoting reference No. 12089/E.D./C.P.

### CREOSOTE FOR BULGARIA.

H.M. Legation at Sofia reports that the Bulgarian State Railways are desirous of receiving tenders for the supply of 500 tons of creosote to the approximate value of 3,500,000 leva. A public adjudication of tenders will be held on the 28th September, 1923.

Reference No. 11456/FE/CC(2).

### QUESTIONNAIRE ON FERTILISERS.

The International Institute of Agriculture, Rome, has issued a questionnaire on Fertilisers, which is to be sent to the Governments of all the adhering States.

The Permanent Committee of the Institute is anxious that suitable measures be taken to increase the production and use of fertilisers in agriculture.

### BRITISH CATALOGUES FOR CANADA.

His Majesty's Senior Trade Commissioner in Canada (Mr. R. W. Dalton) has informed the Department of Overseas Trade that there is a serious lack of British catalogues in the various Trade Commissioners' Offices in Canada. He points out that without such catalogues, it is often a difficult matter to advise firms in Canada as to possible British sources of supply, and that the necessity of referring enquiries to head quarters in London takes time, during which business that might otherwise have gone to British firms, is lost to them.

United Kingdom firms desirous of ensuring their names being given to suitable enquirers should forward copies of their catalogues to any, or all, of the following:—

H.M. Senior Trade Commissioner in Canada, 285, Beaver Hall Hill, Montreal.

H.M. Trade Commissioner, 24, Adelaide Street West, Toronto.

H.M. Trade Commissioner, 210, Winch Building, Vancouver.

The Chief Clerk, Office of H.M. Trade Commissioner, 703, Union Bank Buildings, Winnipeg.

It should be noted that Customs duty is levied on catalogues entering Canada, and firms desiring to send them by parcel post should prepay such duty. For this purpose stamps may be obtained from the office of the High Commissioner for Canada, Kinnaid House, Pall Mall East, London, S.W.1.

### THE SIR JOHN CASS TECHNICAL INSTITUTE, JEWRY STREET, ALDGATE, E.C.3.

SESSION 1923-24.

The session 1923-24 will commence on Thursday, September 20; students will be enrolled on Monday, Tuesday and Wednesday, September 17, 18 and 19, from 6 to 8.30 p.m.

The courses of instruction at the Institute, which are held from 6 to 10 p.m., meet the requirements of those engaged in chemical, metallurgical, electrical, petroleum and the fermentation industries.

Full facilities are provided in the well-equipped laboratories of the Institute for special investigations and research. The instruction in experimental science also provides systematic courses for the examinations of London University, the City and Guilds of London Institute, and of the Institutes of Physics, Chemistry, and Brewing.

Special courses of higher technological instruction form a distinctive feature of the work of the Institute, and during the forthcoming session the following courses will be included in the syllabus:—

Brewing, Malting, Micro-Biology, Bottling and Cellar Management, Petroleum Technology, Colloids, Alternating Currents and Electrical Oscillations, Mathematical Statistics, Metallography and Pyrometry, Heat Treatment, and Mechanical Testing of Metals and Alloys, Foundry Practice, Mining and Surveying.

The Postmaster-General wishes to correct the widespread impression which exists that an initial charge is made for installing a telephone.

During the war a uniform surcharge of £4 on new installations was made; but this charge was abolished more than two years

ago. The present system of charging is broadly as follows: The rental is payable quarterly in advance, and the fees for calls and other services, such as telegrams dictated over subscribers' circuits, are payable quarterly in arrear. On the completion of an installation, a new subscriber pays on account of rental the proportionate amount up to the next quarter day, together with a small deposit in respect of calls to be made during the quarter. The rental includes the cost of installing the telephone, and no other preliminary charge is made on that account.

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### THE INSTITUTE OF METALS.

##### SECOND AUTUMN LECTURE,

Delivered by LIEUT.-COLONEL SIR HENRY FOWLER, K.B.E., at Manchester, on Monday, September 10, 1923, on *The Use of Non-Ferrous Metals in Engineering*.

There are very many articles which every day use has so familiarised us with that we look upon them as common-place. A little thought, however, will show that the fact that we have them available in the form we use them is the result of years of research and patient investigation. It is probable that it was some such thought as this that led the Council of the Institute of Metals to choose the subject of the autumn lecture for this year, and to place it in the hands of an engineer.

The subject itself is so extremely comprehensive that it is only in the form of a popular lecture that it could possibly be dealt with in a single address. It may be said that the use of non-ferrous metals by engineers is the ultimate object of all papers read before the Institute.

Of these metals the one which has been in longest use is copper, and it is at present the one most closely associated either by itself or alloyed with engineering work. The uses to which its comparatively simple alloys with tin and zinc can be put are endless. The next in importance is perhaps tin which, alloyed with copper, lead and antimony, give us those white metals which allow bearings to be a practical proposition.

Aluminium is one of the most interesting of the series of metals and although from an engineering standpoint it is per-

haps most generally used in connection with aeronautics, recent investigations have opened up a new field for its use.

There still remain numbers of other metals which, as alloys, are helping to solve the problems which the advances in recent engineering practice bring in their train.

#### ANNUAL AUTUMN MEETING OF THE INSTITUTE OF METALS, HELD IN MANCHESTER, ON TUESDAY, SEPTEMBER 11, 1923.

*The Cause of Red Stains on Sheet Brass*, by E. A. BOLTON, M.Sc.

The author gave an account of work carried out to elucidate this problem. The various theories which have been from time to time put forward were reviewed and experiments described which bear upon these theories. Although the experiments were carried out in the laboratory, close touch was established throughout with actual works' practice. The outstanding point is that the stains actually occur through reactions of copper oxides in the scale formed during annealing and the pickling medium. Cupric oxide, contrary to the usual opinion, is shown to be as harmful as cuprous oxide.

It is shown that oxides of copper may be present from various causes, such as careless washing after the pickling operation resulting in the presence of acid and salts during the subsequent annealing, the presence of iron in the brass or upon its surface, the use of impure rolling oils, etc. It is concluded, however, that the main cause of the oxidation of the copper is the use of old-fashioned annealing furnaces in which the flames impinge directly upon the brass.

The paper concluded with an account of possible remedies for the red-stain trouble.

*Brinell Hardness Numbers*, by H. W. BROWNSDON, M.Sc., PH.D., F.I.C., Member of Council.

The author drew attention to the desirability of Brinell numbers for non-ferrous metals being given in figures that may be comparable.

*Stereotyping*, by A. H. MUNDEY and JOHN CARTLAND, M.C., M.Sc.

The authors described the process of stereotyping which is generally regarded by printers as one which is almost a trade secret. The authors point out that the process was invented by a practical metallurgist, William Ged, an Edinburgh goldsmith, in 1750.

The metallurgical trials and difficulties were briefly dealt with, and the consideration of metallurgists is invited to some of the problems involved. The authors point out with truth that the industry is much more important than is usually understood, and they call attention to the high degree of accuracy demanded in the mechanical and metallurgical details in order to produce the results which are a commonplace to everyone.

The enormous speed and absolute reliability of production necessary in the case of newspaper work was referred to, in addition to the fact that the product of this metallurgical process—the printed page—is open to the criticism of the whole public.

*Crystallisation Effect on Galvanised Iron Sheets*, by J. D. HANNAH, M.Sc.TECH., and E. L. RHEAD, M.Sc.TECH.

Manufacturers of galvanised iron and steel goods, specially corrugated sheets in which it is desired to obtain the best appearance, have always sought to produce a zinc covered surface having large characteristic spangles. Failure to do this is a frequently recurring source of trouble and loss. The absence of, or the production of, only small spangles has been attributed to many causes. The quality of the steel, either the presence of sulphides and other non-metallic inclusions, or its condition produced by rolling and subsequent treatment, the pickling, either caused by impurities in the acid, by the occlusion of gas by the metal, the temperature of the bath, and the purity of the zinc, have all been blamed for the failures.

Messrs. Hannah and Rhead gave an account of a research to ascertain the real causes. Little assistance can be obtained from literature on the subject.

The research shows that the metal—iron or steel—has practically no influence on the result if the temperatures are satisfactorily maintained. After the conditions of good work had been established samples of both good and bad sheet from which the zinc had been stripped, gave equally good results. It was shown that pure zinc did not yield the desired large spangles, and that too high a temperature interfered with producing large quantities of a zinc iron compound which crystallised in needles on the metal and interfered with the development of the spangle. The presence of tin or aluminium—contrary to expectation and as commonly stated—did not produce the

desired result, but the addition of lead did so immediately.

Judging from the known relationships between zinc and lead, the authors argued that the separation of the impure zinc forming the layer on the metal sheet into conjugate solutions—lead rich and zinc rich—at the dipping temperature, and the method of subsequent crystallisation were the causes of the effects obtained. That this occurred was proved by the analysis of different types of spangle occurring on the same sheet, and by the observed differences in the rate of attack of digerent spangles forming the coating. The separation is attributed to the difference in the surface tensions of the two solutions. That such differences exist was proved by experiment.

Proof of the hypothesis is furnished by the fact that Bismuth, the only common metal that resembles lead more or less, in its relations with zinc, produces similar effects. The temperature at which good results can be obtained is limited by the tendency to form excessive amounts of the iron zinc compound previously referred to, and the time occupied in dipping and cooling.

*Effects of Rate of Cooling on the Density and Composition of Metals and Alloys*, by R. C. READER, PH.D., M.Sc.

This note was concerned chiefly with two rates of cooling, fast and slow, as produced by casting in chill and sand moulds. The results recorded show that the densities of pure metals are not affected by the rate at which they solidify, and a similar remark applies to those alloys which solidify at a constant temperature. In the case, however, of those alloys which solidify over a range of temperature, the rate at which they pass through this range seriously affects the density, the slower the rate of solidification the lower being the density. Also when alloys which possess a long solidifying range are prepared in cylindrical chill moulds they are less dense in the centre than at the outside. Rapid solidification has a pronounced effect on the composition throughout the mass of those alloys which solidify over a range of temperature. When prepared in chill these alloys are found to be richer on the outside in the component of the lower melting point and richer in the centre in the component of the higher melting point. Sand castings in these alloys are uniform throughout. Alloys which solidify at a constant temperature

are uniform in composition throughout, whether prepared in sand or chill moulds.

*The Effect of Small Quantities of Nickel upon High-grade Bearing Metal*, by A. H. MUNDEY and C. C. BISSETT, B.A., B.Sc., B.MET.

This note gave an account of a practical trial of the effect of varying small quantities of nickel upon a tough and well-reputed bearing metal.

There was chosen for test the well known alloy consisting of:

Tin 93 per cent., Antimony 3.5 per cent., Copper 3.5 per cent.

The authors state that nickel is now found to be added to some considerable extent, possibly as a means of identification, but some merit is also claimed for it.

The results of the usual physical tests are detailed. Tensile, compression and hardness tests gave no indication of improvement due to the nickel: in fact, the alloys were rather inferior when containing nickel. Running trials on the Thurston machine on strictly comparative lines showed practically no change as between nickel and non-nickel alloys.

The comparison of hardness at varying increased temperatures exhibited no improvement. Probably the most interesting feature is the structure as shown under the microscope. In the case of the alloy with no nickel the hard copper-tin constituent is very marked in its characteristic crystalline formation. The presence of nickel even in small quantities results in a great diminution of this crystalline structure, and the structure is only in a measure restored by the addition of more copper.

The authors conclude from their experiments that the beneficial results of nickel in alloys of the character employed are yet to be demonstrated.

*The Measurement of the Change of Volume in Metals during Solidification*, by HIKOZO ENDO.

In the casting process it is very important to know to what extent a change of volume occurs during solidification. Notwithstanding this great necessity, the literature concerning the phenomena is very scanty, because of the lack of a suitable method for arriving at an accurate determination. In 1888, Vincentini and Omodei calculated the change of volume of some fusible metals during solidification from the change of density at the melting point. The measurement of the density of different

metals in the vicinity of their melting points has been the subject of inquiry by several investigators among which are to be mentioned E. Wiedemann, Paul Pascal, and Louis Hackspill. M. Toepler, who studied the change of volume by means of a dilatometer, suggested a relation of the change of volume of a metal at melting point to its atomic weight, similar to that of the atomic volume to the atomic weight. Recently K. Bornemann and F. Sauerwald also measured the density of metals at various high temperatures by means of the Archimedes principle, using a mixture of sodium and potassium chlorides as liquid.

The present investigation was started in April, 1921, and the measurement of the change of volume during solidification or melting for a number of metals having low melting points up to 1100° C. has now been finished. This paper contains the results of the measurements, and forms the first report of the results of the investigation of a long series of experiments which are to be extended to other metals having higher melting points.

The method of investigation, which was suggested by Professor K. Honda, consists in the measurement of the change of buoyancy of a metal suspended in an inactive liquid during its solidification or melting by means of a thermobalance.

#### CORRESPONDENCE.

##### THE BRAILLE AND "SERVERS OF THE BLIND" LEAGUE.

To the Editors of THE CHEMICAL NEWS.

SIR,—As the President of the Braille and "Servers of the Blind" League, may I ask the sympathy of your readers for a unique work of help?

Up to the present no provision has been made for the defective blind children—those unfortunate babies who, in addition to blindness, have some other disability, such as backward mentality, deafness, dumbness.

The Braille and "Servers of the Blind" League has undertaken to make this provision, and is establishing the Ellen Terry National Homes for Defective Blind Children, having purchased a home at Reigate, Surrey, where these little children, who are mentally and physically blind, will have the most skilful nursing and treatment, specially adapted educational facilities, and

training in trades suited to their varying capacities.

The Junior Home for children under seven is to do a splendid work, but money is badly needed to pay the mortgage and to obtain the necessary equipment. If funds are provided, the Home can be quickly enlarged to take in more than is at present possible.

Negotiations are taking place for additional homes in the north of England, but the scheme cannot be complete unless the public come to our aid.

Buildings exist in the grounds already purchased which can easily be adapted, if the money can be found for the alterations, for training defectives in light employment suited to their capacities.

The Ministry of Health gives the heartiest welcome and support to our scheme, and is most anxious that we should bring it to an early fruition so as to extend it to the care of adult defectives. In addition, local authorities and blind institutions accord warmest co-operation to our plan, which fills a long-existing need. There is a constant enquiry regarding the admission of double defectives known to them.

No more deserving charity could be found than the kindly care of these little ones—born into the world without light and without hope unless we come to their aid—doubly blind. May I ask for all who feel for these lonely babes—the parents and relatives of those children who are blessed with sight—to share in a great national thank-offering for the power to see by sending their contribution to me at the address of the Braille and "Servers of the Blind" League, 3, Upper Woburn Place, W.C.1.

Thanking you in the name of these little ones,  
Yours sincerely, ELLEN TERRY.



THIS list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Latest Patent Applications.*

21136—Cocksedge, H. E.—Manufacture of sodium carbonate. Aug. 21.

21072—Badische Anilin & Soda Fabrik.—Manufacture of formic acid. Aug. 20.

*Specifications Published this Week.*

202078—Imison, C. S., Bligh, J. A., Wright, R. R., and Carmichael & Co., Ltd., J. F.—Furnaces producing sulphurous gases.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

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Session 1923-24.

(Commencing on Tuesday, 2nd October,  
1923).

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ceived by the 17th September.

JOHN J. JACKSON,

Director of Education,

CITY HALL, CARDIFF.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3310.

[BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE: LIVERPOOL, 1923.]

## THE PRESIDENTIAL ADDRESS. THE ELECTRICAL STRUCTURE OF MATTER.

BY PROFESSOR SIR ERNEST RUTHERFORD,  
D.SC., LL.D., PH.D., F.R.S.,

*President of the Association.*

*(Continued from Page 165.)*

We must now look back again to the earlier stages of the present epoch in order to trace the development of our ideas on the detailed structure of the atom. That electrons as such were important constituents was clear by 1900, but little real progress followed until the part played by the positive charges was made clear. New light was thrown on this subject by examining the deviation of  $\alpha$  particles when they passed through the atoms of matter. It was found that occasionally a swift particle was deflected from its rectilinear path through more than a right angle by an encounter with a single atom. In such a collision the laws of dynamics ordinarily apply, and the relation between the velocities of the colliding atoms before and after collision are exactly the same as if the two colliding particles are regarded as perfectly elastic spheres of minute dimensions. It must, however, be borne in mind that in these atomic collisions there is no question of mechanical impacts such as we observe with ordinary matter. The reaction between the two particles occurs through the intermediary of the powerful electric fields that surround them. Beautiful photographs illustrating the accuracy of these laws of collision between an  $\alpha$  particle and an atom have been obtained by Messrs. Wilson, Blackett, and others, while Mr. Wilson has recently obtained many striking illustrations of collisions between two electrons. Remembering the great kinetic energy of the  $\alpha$  particle, its deflection through a large angle in a single atomic encounter shows clearly that very intense deflecting forces exist inside the atom. It seemed clear that electric fields of the required magnitude could be obtained only if

the main charge of the atom were concentrated in a minute nucleus. From this arose the conception of the nuclear atom, now so well known, in which the heart of the atom is supposed to consist of a minute but massive nucleus, carrying a positive charge of electricity, and surrounded at a distance by the requisite number of electrons to form a neutral atom.

A detailed study of the scattering of  $\alpha$  particles at different angles, by Geiger and Marsden, showed that the results were in close accord with this theory, and that the intense electric forces near the nucleus varied according to the ordinary inverse square law. In addition, the experiments allowed us to fix an upper limit for the dimensions of the nucleus. For a heavy atom like that of gold the radius of the nucleus, if supposed to be spherical, was less than one-thousandth of the radius of the complete atom surrounded by its electrons, and certainly less than  $4 \times 10^{-12}$  cms. All the atoms were found to show this nuclear structure, and an approximate estimate was made of the nuclear charge of different atoms. This type of nuclear atom, based on direct experimental evidence, possesses some very simple properties. It is obvious that the number of units of resultant positive charge in the nucleus fixes the number of the outer planetary electrons in the neutral atom. In addition, since these outer electrons are in some way held in equilibrium by the attractive forces from the nucleus, and, since we are confident from general physical and chemical evidence that all atoms of any one element are identical in their external structure, it is clear that their arrangement and motion must be governed entirely by the magnitude of the nuclear charge. Since the ordinary chemical and physical properties are to be ascribed mainly to the configuration and motion of the outer electrons, it follows that the properties of an atom are defined by a whole number representing its nuclear charge. It thus becomes of great importance to determine the value of this nuclear charge for the atoms of all the elements.

Data obtained from the scattering of  $\alpha$  particles, and also from the scattering of X-rays by light elements, indicated that the nuclear charge of an element was numerically equal to about half the atomic weight in terms of hydrogen. It was fairly clear from general evidence that the hydrogen nucleus had a charge one, and the

helium nucleus (the  $\alpha$  particle) a charge two. At this stage another discovery of great importance provided a powerful method of attack on this problem. The investigation by Laue on the diffraction of X-rays by crystals had shown definitely that X-rays were electromagnetic waves of much shorter wave-length than light, and the experiments of Sir William Bragg and W. L. Bragg had provided simple methods for studying the spectra of a beam of X-rays. It was found that the spectrum in general shows a continuous background on which is superimposed a spectrum of bright lines. At this stage H. G. J. Moseley began a research with the intention of deciding whether the properties of an element depended on its nuclear charge rather than on its atomic weight as ordinarily supposed. For this purpose the X-ray spectra emitted by a number of elements were examined and found to be all similar in type. The frequency of a given line was found to vary very nearly as the square of a whole number which varied by unity in passing from one element to the next. Moseley identified this whole number with the atomic or ordinal number of the elements when arranged in increasing order of atomic weight, allowance being made for the known anomalies in the periodic table and for certain gaps corresponding to possible but missing elements. He concluded that the atomic number of an element was a measure of its nuclear charge, and the correctness of this deduction has been recently verified by Chadwick by direct experiments on the scattering of  $\alpha$  particles. Moseley's discovery is of fundamental importance, for it not only fixes the number of electrons in all the atoms, but shows conclusively that the properties of an atom, as had been surmised, are determined not by its atomic weight but by its nuclear charge. A relation of unexpected simplicity is thus found to hold between the elements. No one could have anticipated that with few exceptions all atomic numbers between hydrogen 1, and uranium 92, would correspond to known elements. The great power of Moseley's law in fixing the atomic number of an element is well illustrated by the recent discovery by Coster and Hevesy in Copenhagen of the missing element of atomic number 72, which they have named "hafnium."

Once the salient features of the structure of atoms have been fixed and the number of electrons known, the further study of the structure of the atom falls naturally

into two great divisions: one, the arrangement of the outer electrons which controls the main physical and chemical properties of an element, and the other the structure of the nucleus on which the mass and radioactivity of the atom depends. On the nuclear theory the hydrogen atom is of extreme simplicity, consisting of a singly-charged positive nucleus with only one attendant electron. The position and motions of the single electron must account for the complicated optical spectrum, and whatever physical and chemical properties are to be attributed to the hydrogen atom. The first definite attack on the problem of the electronic structure of the atom was made by Niels Bohr. He saw clearly that, if this simple constitution was assumed, it is impossible to account for the spectrum of hydrogen on the classical electrical theories, but that a radical departure from existing views was necessary. For this purpose he applied to the atom the essential ideas of the Quantum Theory which had been developed by Planck for other purposes, and had been found of great service in explaining many fundamental difficulties in other branches of science. On Planck's theory radiation is emitted in definite units or quanta, in which the energy  $E$  of a radiation is equal to  $h\nu$  where  $\nu$  is the frequency of the radiation measured by the ordinary methods and  $h$  is a universal constant. This quantum of radiation is not a definite fixed unit like the atom of electricity, for its magnitude depends on the frequency of the radiation. For example, the energy of a quantum is small for visible light, but becomes large for radiation of high frequency corresponding to the X-rays or the  $\gamma$  rays from radium.

Time does not allow me to discuss the underlying meaning of the quantum theory or the difficulties connected with it. Certain aspects of the difficulties were discussed in the Presidential Address before this Association by Sir Oliver Lodge at Birmingham in 1913. It suffices to say that this theory has proved of great value in several branches of science, and is supported by a large mass of direct experimental evidence.

In applying the quantum theory to the structure of the hydrogen atom, Bohr supposed that the single electron could move in a number of stable orbits, controlled by the attractive force of the nucleus, without losing energy by radiation. The position and character of these orbits were defined by certain quantum relations depending on

one or more whole numbers. It was assumed that radiation was only emitted when the electron for some reason was transferred from one stable orbit to another of lower energy. In such a case it was supposed that a homogeneous radiation was emitted of frequency  $\nu$  determined by the quantum relation  $E=h\nu$ , where  $E$  was the difference of the energy of the electron in the two orbits. Some of these possible orbits are circular, others elliptical, with the nucleus as a focus, while if the change of mass of the electron with velocity is taken into account the orbits, as Sommerfeld showed, depend on two quantum numbers, and are not closed, but consist of a nearly elliptical orbit slowly rotating round the nucleus. In this way it is possible not only to account for the series relations between the bright lines of the hydrogen spectrum, but also to explain the fine structure of the lines and the very complicated changes observed when the radiating atoms are exposed in a strong magnetic or electric field. Under ordinary conditions the electron in the hydrogen atom rotates in a circular orbit close to the nucleus, but if the atoms are excited by an electric discharge or other suitable method, the electron may be displaced and occupy any one of the stable positions specified by the theory. In a radiating gas giving the complete hydrogen spectrum there will be present many different kinds of hydrogen atoms, in each of which the electron describes one of the possible orbits specified by the theory. On this view it is seen that the variety of modes of vibration of the hydrogen atom is ascribed, not to complexity of the structure of the atom, but to the variety of stable orbits which an electron may occupy relative to the nucleus. This novel theory of the origin of spectra has been developed so as to apply not only to hydrogen but to all the elements, and has been instrumental in throwing a flood of light on the relations and origin of their spectra, both X-ray and optical. The information thus gained has been applied by Bohr to determine the distribution of the electrons round the nucleus of any atom. The problem is obviously much less complicated for hydrogen than for a heavy atom, where each of the large number of electrons present acts on the other, and where the orbits described are much more intricate than the orbit of the single electron in hydrogen. Notwithstanding the great difficulties of such a complicated system of electrons in motion, it has

been possible to fix the quantum numbers that characterise the motion of each electron, and to form at any rate a rough idea of the character of the orbit.

These planetary electrons divide themselves up into groups, according as their orbits are characterised by one or more equal quantum numbers. Without going into detail, a few examples may be given to illustrate the conclusions which have been reached. As we have seen, the first element, hydrogen, has a nuclear charge of 1 and 1 electron; the second, helium, has a charge 2 and 2 electrons, moving in coupled orbits on the detailed nature of which there is still some uncertainty. These two electrons form a definite group, known as the K group, which is common to all the elements except hydrogen. For increasing nuclear charge the K group of electrons retain their characteristics, but move with increasing speed, and approach closer to the nucleus. As we pass from helium of atomic number 2 to neon, number 10, a new group of electrons is added consisting of two sub-groups, each of four electrons, together called the L group. This L group appears in all atoms of higher atomic number, and, as in the case of the K group, the speed of motion of the electrons increases, and the size of their orbits diminishes with the atomic number. When once the L group has been completed, a new and still more complicated M group of electrons begins forming outside it, and a similar process goes on until uranium, which has the highest atomic number, is reached.

It may be of interest to try to visualise the conception of the atom we have so far reached by taking for illustration the heaviest atom, uranium. At the centre of the atom is a minute nucleus surrounded by a swirling group of 92 electrons, all in motion in definite orbits, and occupying but by no means filling a volume very large compared with that of the nucleus. Some of the electrons describe nearly circular orbits round the nucleus; others, orbits of a more elliptical shape whose axes rotate rapidly round the nucleus. The motion of the electrons in the different groups is not necessarily confined to a definite region of the atom, but the electrons of one group may penetrate deeply into the region mainly occupied by another group, thus giving a type of inter-connection or coupling between the various groups. The maximum speed of any electron depends on the closeness of the approach to the nucleus, but

the outermost electron will have a minimum speed of more than 1,000 kilometres per second, while the innermost K electrons have an average speed of more than 150,000 kilometres per second, or half the speed of light. When we visualise the extraordinary complexity of the electronic system we may be surprised that it has been possible to find any order in the apparent medley of motions.

In reaching these conclusions, which we owe largely to Professor Bohr and his co-workers, every available kind of data about the different atoms has been taken into consideration. A study of the X-ray spectra, in particular, affords information of great value as to the arrangement of the various groups in the atom, while the optical spectrum and general chemical properties are of great importance in deciding the arrangements of the superficial electrons. While the solution of the grouping of the electrons proposed by Bohr has been assisted by considerations of this kind, it is not empirical in character, but has been largely based on general theoretical considerations of the orbits of electrons that are physically possible on the generalised quantum theory. The real problem involved may be illustrated in the following way. Suppose the gold nucleus be in some way stripped of its attendant seventy-nine electrons, and that the atom is reconstituted by the successive addition of electrons one by one. According to Bohr, the atom will be reorganised in one way only, and one group after another will successively form and be filled up in the manner outlined. The nucleus atom has often been likened to a solar system where the sun corresponds to the nucleus and the planets to the electrons. The analogy, however, must not be pressed too far. Suppose, for example, we imagined that some large and swift celestial visitor traverses and escapes from our solar system without any catastrophe to itself or the planets. There will inevitably result permanent changes in the lengths of the month and year, and our system will never return to its original state. Contrast this with the effect of shooting an electron or a particle through the electronic structure of the atom. The motion of many of the electrons will be disturbed by its passage, and in special cases an electron may be removed from its orbit and hurled out of its atomic system. In a short time another electron will fall into the vacant place from one of the outer groups, and this vacant place in turn will be filled

up, and so on until the atom is again reorganised. In all cases the final state of the electronic system is the same as in the beginning. This illustration also serves to indicate the origin of the X-rays excited in the atom, for these arise in the process of reformation of an atom from which an electron has been ejected, and the radiation of highest frequency arises when the electron is removed from the K group.

It is possibly too soon to express a final opinion on the accuracy of this theory which defines the outer structure of the atom, but there can be no doubt that it constitutes a great advance. Not only does it offer a general explanation of the optical and X-ray spectra of the atom, but it accounts in detail for many of the most characteristic features of the periodic law of Mendeléef. It gives us for the first time a clear idea of the reason for the appearance in the family of elements of groups of consecutive elements with similar chemical properties, such as the groups analogous to the iron group and the unique group of rare earths. The theory of Bohr, like all living theories, has not only correlated a multitude of isolated facts known about the atom, but has shown its power to predict new relations which can be verified by experiment. For example, the theory predicted the relations which must subsist between the Rydberg constants of the arc and spark spectra, and generally between all the successive optical spectra of an element, a prediction so strikingly confirmed by Paschen's work on the spectrum of doubly ionised aluminium and Fowler's work on the spectrum of trebly ionised silicon. Finally, it predicted with such great confidence the chemical properties of the missing element, number 72, that it gave the necessary incentive for its recent discovery.

While the progress of our knowledge of the outer structure of atoms has been much more rapid than could have been anticipated, we clearly see that only a beginning has been made on this great problem, and that an enormous amount of work is still required before we can hope to form anything like a complete picture even of the outer structure of the atom. We may be confident that the main features of the structure are clear, but in a problem of such great complexity progress in detail must of necessity be difficult and slow.

We have not so far referred to the very difficult question of the explanation on this theory of the chemical combination of

atoms. In fact, as yet the theory has hardly concerned itself with molecular structure. On the chemical side, however, certain advances have already been made, notably by G. N. Lewis, Kossel, and Langmuir, in the interpretation of the chemical evidence by the idea of shared electrons, which play a part in the electronic structure of two combined atoms. There can be little doubt that the next decade will see an intensified attack by physicists and chemists on this very important but undoubtedly very complicated question.

Before leaving this subject, it may be of interest to refer to certain points in Bohr's theory of a more philosophical nature. It is seen that the orbits and energies of the various groups of electrons can be specified by certain quantum numbers, and the nature of the radiation associated with a change of orbit can be defined. But at the same time we cannot explain why these orbits are alone permissible under normal conditions, or understand the mechanism by which radiation is emitted. It may be quite possible to formulate accurately the energy relation of the electrons in the atom on a simple theory, and to explain in considerable detail all the properties of an atom, without any clear understanding of the underlying processes which lead to these results. It is natural to hope that with advance of knowledge we may be able to grasp the details of the process which leads to the emission of radiation, and to understand why the orbits of the electrons in the atom are defined by the quantum relations. Some, however, are inclined to take the view that in the present state of knowledge it may be quite impossible in the nature of things to form that detailed picture in space and time of successive events that we have been accustomed to consider as so important a part of a complete theory. The atom is naturally the most fundamental structure presented to us. Its properties must explain the properties of all more complicated structures, including matter in bulk, but we may not, therefore, be justified in expecting that its processes can be explained in terms of concepts derived entirely from a study of molar properties. The atomic processes involved may be so fundamental that a complete understanding may be denied us. It is early yet to be pessimistic on this question, for we may hope that our difficulties may any day be resolved by further discoveries.

We must now turn our attention to that

new and comparatively unexplored territory, the nucleus of the atom. In a discussion on the structure of the nucleus, I was rash enough to say that it was a problem that might well be left to the next generation, for at that time there seemed to be few obvious methods of attack to throw light on its constitution. While much more progress has been made than appeared possible at that time, the problem of the structure of the nucleus is inherently more difficult than the allied problem already considered of the structure of the outer atom, where we have a wealth of information obtained from the study of light and X-ray spectra and from the chemical properties to test the accuracy of our theories.

In the case of the nucleus, we know its resultant charge, fixed by Moseley's law, and its mass, which is very nearly equal to the mass of the whole atom, since the mass of the planetary electrons is relatively very small and may for most purposes be neglected. We know that the nucleus is of size minute compared with that of the whole atom, and can with some confidence set a maximum limit to its size. The study of radioactive bodies has provided us with very valuable information on the structure of the nucleus, for we know that the  $\alpha$  and  $\beta$  particles must be expelled from it, and there is strong evidence that the very penetrating  $\gamma$  rays represent modes of vibration of the electrons contained in its structure. In the long series of transformations which occur in the uranium atom, eight  $\alpha$  particles are emitted and six electrons, and it seems clear that the nucleus of a heavy atom is built up, in part at least, of helium nuclei and electrons. It is natural to suppose that many of the ordinary stable atoms are constituted in a similar way. It is a matter of remark that no indication has been obtained that the lightest nucleus, viz., that of hydrogen, is liberated in these transformations, where the processes occurring are of so fundamental a character. At the same time, it is evident that the hydrogen nucleus must be a unit in the structure of some atoms, and this has been confirmed by direct experiment. Dr. Chadwick and I have observed that swift hydrogen nuclei are released from the elements boron, nitrogen, fluorine, sodium, aluminium, and phosphorus when they are bombarded by swift  $\alpha$  particles, and there is little room for doubt that these hydrogen nuclei form an essential part of the nuclear structure. The

speed of ejection of these nuclei depends on the velocity of the  $\alpha$  particle and on the element bombarded. It is of interest to note that the hydrogen nuclei are liberated in all directions, but the speed in the backward direction is always somewhat less than in the direction of the  $\alpha$  particle. Such a result receives a simple explanation if we suppose that the hydrogen nuclei are not built into the main nucleus but exist as satellites probably in motion round a central core. There can be no doubt that bombardment by  $\alpha$  particles has effected a veritable disintegration of the nuclei of this group of elements. It is significant that the liberation of hydrogen nuclei only occurs in elements of odd atomic number, viz., 5, 7, 9, 11, 13, 15, the elements of even number appearing quite unaffected. For a collision of an  $\alpha$  particle to be effective, it must either pass close to the nucleus or actually penetrate its structure. The chance of this is excessively small on account of the minute size of the nucleus. For example, although each individual  $\alpha$  particle will pass through the outer structure of more than 100,000 atoms of aluminium in its path, it is only about one  $\alpha$  particle in a million that gets close enough to the nucleus to effect the liberation of its hydrogen satellite.

(To be continued.)

[BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.—SECTIONAL TRANSACTIONS.]

SECTION A.—MATHEMATICAL AND PHYSICAL SCIENCE.

THURSDAY, SEPTEMBER 13.

PROF. C. G. DARWIN, F.R.S.—*The Recent Work of Prof. A. H. Compton on the Scattering of X-rays.*

PROF. C. G. BARKLA, F.R.S.—*X-ray Absorption and the J Discontinuities.*

DR. W. M. SMART.—*Navigation.*

FRIDAY, SEPTEMBER 14.

SENATORE VITO VOLTERRA, FOR. MEM. R.S.—*Liquid Jets.*

PROF. R. A. MILLIKAN.—*The Penetrating Radiations from the Upper Air.*

SIR OLIVER LODGE, F.R.S.—*Matter and Radiation.*

MR. G. STEAD and MISS B. TREVELYAN.—*The Production of Triatomic Hydrogen (?)*.

Hydrogen is subjected to intense electronic bombardment in a cylindrical thermionic tube with open grid and no anode. With a grid potential of 30 volts and over, a blue glow, consisting of primary and secondary hydrogen lines, is observed near the filament. The glow spreads progressively along the tube, the current increasing similarly till it suddenly falls to a small value, and the glow simultaneously runs back. A regular oscillation of the glow and current is maintained, and the pressure in the tube follows the current changes.

It appears that a polymerised modification of hydrogen is periodically formed and decomposed. If a tube surrounded by liquid air is attached no oscillation takes place, but nearly all the gas disappears rapidly. It is re-liberated on removing the liquid air, and is stable, but easily decomposed by electric discharge, showing an increase in volume in the ratio of 1.5 to 1. The decomposed gas shows bright primary and secondary spectra of hydrogen. The optimum pressure in the tube is about 0.05 mm. of mercury.

CAPT. D. BRUNT.—*Energy of the Circulation of the Atmosphere.*

MR. F. J. W. WHIPPLE.—*Notes on the Transmission of Sound through the Atmosphere.*

DR. A. T. DOODSON.—*Meteorological Effects on Sea Level and Tides.*

MR. T. SMITH.—*Apocoptic Expansions.*

PROF. H. LEVY and MR. W. H. MOORE.—*Notes on the Approximate Expression of Empirical Results.*

REV. A. L. CORTIE.—*Series in Magnetic Disturbances.*

MR. W. M. MORDEY.—*Some Recent Studies in Alternating Magnetism.* (Illustrated by Experiments and Lantern Slides).

MR. S. G. BROWN, F.R.S.—*Demonstration of the 'Frenophone,' or Friction Operated Loud-Speaker.*

MONDAY, SEPTEMBER 17.

PRESIDENTIAL ADDRESS, by PROF. J. C. McLENNAN, F.R.S., on *Origin of Spectra* (an account of which will be published subsequently in *The Chemical News*).

PROF. N. BOHR.—*The Correspondence Principle*.

The quantum theory of atomic constitution rests upon the following two postulates:—

I.—Among the conceivably possible states of motion in an atomic system there exist a number of so-called "stationary states" which, in spite of the fact that the motion of the particles in these states obeys the laws of classical mechanics to a considerable extent, possess a peculiar mechanically unexplainable stability, of such a sort that every permanent change in the motion of the system must consist of a complete transition from one stationary state to another.

II.—While in contradiction to the classical electromagnetic theory no radiation takes place from the atom in the stationary states themselves, a process of transition between two stationary states can be accompanied by the emission of electromagnetic radiation, which will have the same properties as that which would be sent out according to the classical theory from an electrified particle executing a harmonic vibration with constant frequency. This frequency  $\nu$  has, however, no simple relation to the motion of the particles of the atom, but is given by the quantum relation

$$h\nu = E' - E'', \quad (1)$$

where  $h$  is Planck's constant, and  $E'$  and  $E''$  are the values of the energy of the atom in the two stationary states that form the initial and final states of the radiation process.

It will be the purpose of these remarks to show how, notwithstanding the fundamental departure from the ideas of the classical theories of mechanics and electrodynamics involved in these postulates, it has been possible to trace a connection between the radiation emitted by an atom and the motion of the particles which exhibits a far-reaching analogy to that claimed by the classical ideas of the origin of radiation.

It was shown by examples from the investigation of the spectra of the elements and of the effects of electric and magnetic fields on spectral lines, how the correspondence principle has been supported to an extent that seems to justify us in using it as a guide also in more complicated cases, which we meet in the theory of atomic constitution, and where it has not yet been possible to fix the stationary states in an unambiguous way by use of symbols borrowed from classical mechanics.

PROF. P. EHRENFEST. — *Remarks on Quantisation*.

PROF. P. LANGEVIN.—*The Structure of Atoms and their Magnetic Properties*.

To account for magnetic properties it is assumed that each atom or molecule normally possesses a definite magnetic moment proportional to the total moment of the quantity of electron movement. This can be zero when the symmetry of the edifice is sufficient, and always becomes modified in the diamagnetic sense under the action of an external field.

The laws of quanta allow us to predict the existence of molecular magnetic moments which are integral multiples of the Bohr magneton, and they alone permit us to develop coherently an electronic theory of magnetism in the same way as they have rendered possible a theory of atomic structure and of the emission of spectra.

PROF. R. W. WOOD, FOR. MEM. R.S., and DR. A. ELLETT.—*The Effects of Weak Magnetic Fields on the Polarisation of Resonance Radiation*.

MR. I. O. GRIFFITH.—*Experiments in very High Temperatures*.

TUESDAY, SEPTEMBER 18.

Discussion on *The Spectra of the Lighter Elements*. Opener, the President, PROF. J. C. McLENNAN, F.R.S. Speakers: Prof. N. Bohr, Prof. R. A. Millikan, Prof. A. Fowler, F.R.S., and others.

DR. F. W. ASTON, F.R.S.—*Further Determinations of the Constitution of the Elements by the method of Accelerated Anode Rays*.

MR. R. W. ROBERTS.—*The Magnetic Rotary Dispersion in certain Paramagnetic Liquids*.

MR. R. ABLETT.—*The Angle of Contact—Variation with Relative Motion of Solid and Liquid.*

Report of the Seismology Committee.

## SECTION B.—CHEMISTRY.

THURSDAY, SEPTEMBER 13.

JOINT DISCUSSION with Sections A and G (in rooms of Section B), on *Cohesion and Molecular Forces*. SIR WILLIAM H. BRAGG, F.R.S., DR. W. ROSENHAIN, F.R.S., DR. A. A. GRIFFITH, and other speakers.

PROF. SVEN ODEN.—*The Formation of Precipitates.*

PROF. G. S. WHITBY.—*The Nature and Significance of the Resin of Hevea Rubber.*

The resin of raw rubber, which constitutes about 3 per cent. of the material, contains liquid unsaturated acids, a new solid fatty acid (Heveic acid), a phytosterol glucoside, a phytosterol ester, a free phytosterol, quebrachitol, and *d*-valine. The acids have a marked influence on the vulcanisation of rubber in the presence of catalysts. The introduction into the rubber of strong bases increases the rate of vulcanisation with catalysts and enhances the tensile strength of the product. This effect is not due merely or mostly to the elimination, by neutralisation, of the retarding influence of acids, but largely to the dispersing action on the caoutchouc of the soaps produced. The total resin-acid-content of different samples of raw rubber varies greatly. Such variation is probably an important factor in vulcanisation. The ability of organic substances to swell rubber was studied in relation to the question of the mode of occurrence of the resin constituents in latex and in rubber.

FRIDAY, SEPTEMBER 14.

PRESIDENTIAL ADDRESS, by PROF. F. G. DONNAN, F.R.S., on *The Physical Chemistry of Interfaces* (an account of which will be published later in *The Chemical News*).

PROF. G. N. LEWIS.—*The Quantum Theory in Chemistry.*

DR. N. V. SIDGWICK, F.R.S.—*The Bohr Atom and the Periodic Law.*

DR. D. COSTER.—*On High Frequency Spectra and the Theory of Atomic Structure.*

Moseley showed that the characteristic X-ray spectra have a very simple structure. The square root of the frequency of a given X-ray line is a linear function of the atomic number. The great changes in physical and chemical properties, which mostly occur when proceeding from one element to the next one in the periodic table, are not expressed in the X-ray spectrum.

Recent researches have revealed that some peculiarities of the periodic table find expression in the X-ray spectrum. If we plot Moseley curves not for the lines themselves but for the spectral terms, we observe at different stages sudden changes in the slope of the curves. These irregularities correspond with regions of the periodic table where, according to Bohr, an inner group of electrons is being completed.

Recently X-ray spectroscopy has led to a confirmation of the Bohr theory. According to Bohr, the element of atomic number 72 should not belong to the rare earth metals, but must be a homologue of zirconium. This is verified by the discovery of hafnium.

MISS EDITH H. USHERWOOD.—*The Activation of Hydrogen in Organic Compounds.*

A great variety of organic chemical phenomena depend upon one and the same molecular condition. This condition is defined in terms of molecular structure, and the result follows that tendency to undergo reactions of many different kinds is referred to certain definite and easily recognised structural features.

JOINT DISCUSSION with Section I (in the rooms of Section B), on *The Physical Chemistry of Membranes in Relation to Physiological Science*. PROF. H. E. ROAF, PROF. F. G. DONNAN, and other speakers.

DR. E. B. R. PRIDEAUX.—*Membrane Potentials considered as Diffusion Potentials.*

Through most ordinary membranes, such as parchment, a slow diffusion of electrolyte takes place, and the membrane potentials at these are not due to the impermeability, but to the selective permeability, of either anion or cation. These potentials are generally higher than the corresponding diffusion potentials, and may be considered as diffusion potentials in which



the transport numbers or the relative mobilities of one ion are modified by the membrane. A comparison of the mobility of the anion in the case of Na and K benzoates and salicylate determined by conductivity with the present measurements of diffusion potentials, viscosities, and membrane potentials, shows that the mobility of the benzoic anion has indeed been diminished by the parchment to a value which is apparently definite both for K and for Na salts. The mobility of the salicylic ion was diminished in a higher ratio.

MONDAY, SEPTEMBER 17.

DR. E. F. ARMSTRONG, F.R.S.—*Enzymes*.

Enzymes are to be regarded as colloid catalysts. It is customary to think of them as definite chemical entities, but the activity associated with them is connected with certain aggregates of groups in a very much larger molecule. Probably the enzyme, as such, is incapable of existing, and the larger molecule may well be variable in its nature. Their activity in the main is hydrolytic—that is, they activate water molecules, and in special cases they also bring about synthetic action; there is also the class of oxidising and reducing enzymes which act again in activating water so as to give oxygen to one and hydrogen to another acceptor. The study of enzymes is thus intimately bound up with that of the behaviour of water in solutions.

Enzymes are obtained from animal and vegetable tissues in a concentrated, as opposed to a purified, condition; their outstanding and indeed remarkable property is their very highly specific character. In every instance their action is restricted to one or to a few substances very closely related in structure, and there is obviously the most intimate correlation between the structure of the substrate and of the enzyme complex.

DR. K. G. FALK.—*The Relation of Certain Enzyme Actions to Tissue Differentiation and Tumour Growth*.

The comparative lipase actions on a number of different esters and protease actions on several protein preparations, of different tissues and organs of rats as well as of the Flexner-Jobling rat carcinoma, were studied. Well-defined differences in the actions were found. A number of tumours of human origin and some normal human tissues were studied similarly. A more

complete study of the enzyme actions of fibromyoma of the uterus indicated in some cases enzyme actions of the growths similar to those of uterus muscle, and in some cases both types of actions present in the material obtained from different parts of the same specimen. The enzyme results corresponded to the histological examinations of the same materials.

MR. W. G. PALMER.—*Catalytic Actions in the System Copper, Copper-Oxide, Oxygen, and Gaseous Reducing Agent*.

The rate of oxidation of a copper film  
1  
about — mm. in thickness can readily be  
1000

found from observations on the increasing electrical resistance; similarly the rate of reduction of oxide can be followed by observing the decrease of resistance. Such a film conducts electricity normally, but is sufficiently thin for the effects of gaseous diffusion to be absent.

Mixtures of reducing gas (such as carbon monoxide or hydrogen) with oxygen, when brought into contact with copper at 250° C., oxidise the metal more rapidly than does pure oxygen. This effect is very marked even when equal volumes of reducing gas and oxygen are used. The reduction of copper oxide by carbon monoxide or by hydrogen at low temperatures takes place only in the presence of copper, and the rate of reduction is simply proportional to the amount of metal present.

When hydrogen is used for reduction the water formed acts as a "negative" catalyst, and the reduction is soon brought to a standstill unless the water is removed by exhaustion.

PROF. W. VERNADSKY.—*Alumosilicates*.

We can distinguish in alumosilicates bodies of different chemical functions:

anhydrides:  $\text{Al}_2\text{SiO}_5$  sillimanite  
 $\text{Al}_2\text{Si}_2\text{O}_7$  leverrierite  
 $\text{Al}_2\text{SiO}_4\text{F}_2$  topaz, &c.  
acids:  $\text{H}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot \text{H}_2\text{O}$ —kaolinite  
 $\text{H}_2\text{Al}_2\text{Si}_4\text{O}_{12}$ —pyrophyllite, &c.  
salts:  $\text{K}_2\text{Al}_2\text{Si}_6\text{O}_{16}$ —orthoclase, &c.

All these bodies in the solid condition can give addition products, e.g.,

zoisite  $3\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot \text{Ca}(\text{OH})_2$   
grossularite  $\text{CaAl}_2\text{Si}_2\text{O}_8 \cdot \text{Ca}_2\text{SiO}_4$   
where the alumosilicate group dominates the properties of the compound,

the salts and their addition products can be divided into *three groups*:

1.—*Sillimanite salts*—of acid  $\text{H}_2\text{Al}_2\text{SiO}_5$  and their addition products: group of *chloritoids*.

2.—*Leverrierite salts*—of acids  $\text{H}_2\text{Al}_2\text{Si}_2\text{O}_8 + n\text{O}_8 + 2$   $n = 0, 2, 4, 6, 8$ .  
 $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$ —phacellite  
 $\text{K}_2\text{Al}_2\text{Si}_4\text{O}_{12}$ —leucite.

These compounds have a chromogene constitution.

3.—*Salts of polybasic acids* of anhydrides  $\text{Al}_2\text{SiO}_5$ ,  $\text{Al}_2\text{Si}_2\text{O}_7$ ,  $\text{Al}_2\text{Si}_4\text{O}_9$  . . .  
 $\text{Al}_2\text{SiO}_5 - n(\text{HO})_2$   
 $\text{Al}_2\text{Si}_2\text{O}_7 - n(\text{HO})_2$

#### *Chlorites*

Mostly hydrated Mg and Fe compounds.

DR. G. HEVESY.—*The Chemistry of Hafnium*.

Though hafnium is placed in the periodic table between zirconium and thorium, its chemical properties are not intermediate between those of zirconium and thorium, but much nearer to Zr.

While the fluorides and double fluorides of thorium are practically insoluble, the corresponding zirconium compounds, and still more the hafnium compounds, are fairly soluble in cold, very soluble in hot water. By this method zirconium can easily be separated from hafnium. The mineral is melted with  $\text{KFHF}$ , and by crystallising the potassium double fluorides the hafnium concentrates in the mother-liquor.

Hafnium oxalate is soluble in excess of oxalic acid. The oxychloride is less soluble than zirconium oxychloride. Hafnium is more basic than zirconium; accordingly the latter is more easily precipitated by ammonia, sodium thiosulphate, &c.; and while zirconium sulphate begins to decompose above  $400^\circ$ , the temperature at which hafnium sulphate undergoes marked decomposition lies about  $100^\circ$  higher. Thorium phosphate is easily dissolved by strong acids, zirconium phosphate much less, whereas hafnium phosphate is found to be still less soluble.

Zirconium extracted from different minerals always contains  $\frac{1}{3}$ -30 per cent. hafnium. We must conclude that "zirconium," hitherto thought to be an element, is a mixture of zirconium and hafnium.

TUESDAY, SEPTEMBER 18.

SENATORE GINORI CONTI.—*The Utilisation of Volcanic Steam*. (With lantern slides.)

MISS ELIZABETH S. SEMMENS.—*The Biochemical Effect of Polarised Light*.

That plane polarised light has a distinct accelerating effect on the breaking up of starch grains in the presence of diastase can be shown under the microscope. At laboratory temperatures below  $20^\circ$  and with small concentration of diastase, starch grains exposed to light polarised by reflection or by a Nicol prism erode quickly and give crystals of sugar, controls in ordinary light or in the dark remaining almost intact.

DR. R. G. FARGHER.—*Cotton Wax*.

The term "cotton wax" has been applied by different writers to the extracts obtained from cotton by means of organic solvents, and even to the material removed by boiling the cotton with dilute sodium hydroxide. It includes fat, wax, and the more readily soluble portion of the resin present in the cotton, the proportion of fat being relatively small.

Comparison of the extracts obtained with a number of organic solvents indicated that carbon tetrachloride removed the fat and wax and left the major portion of the resin undissolved; whilst chloroform dissolved fat, wax and resin.

DR. D. A. CLIBBENS.—*The Absorption of Methylene Blue by Cotton*.

A quantitative investigation of the conditions which determine the absorption of methylene blue by bleached cotton from neutral solutions of methylene blue hydrochloride. The object of the work was to provide a method for determining the efficiency of cotton-bleaching processes with respect to their production of pure cotton cellulose. Measurements of the absorption of methylene blue at various stages of a bleaching process show:—

The absorption by raw cotton is high, and is a property of certain acidic non-cellulose impurities.

The absorption diminishes progressively, and measures the progressive purification of the cotton cellulose.

The absorption by scoured cotton is not further affected by normal bleaching, agents, so-called "over-bleaching," causes chemical attack of the cellulose itself and though excessive treatment with oxidising results in an increased absorption of the basic dye due to the presence of acidic oxidation products ("oxycellulose").

PROF. H. E. FIERZ.—*The Sulphonation and Nitration of Naphthalene.*

The author has investigated the interaction of naphthalene and sulphuric acid, and has been able to show that the rule established first by Armstrong and Wynne holds good in every case where the system naphthalene and sulphuric acid is involved.

Several free naphthalene-mono and disulphonic acids and nitration products have been prepared and described. The crystals were measured and compared with the corresponding metal salts. Over 100 were investigated.

GENERAL NOTES.

PRODUCTION OF METALS OF THE PLATINUM GROUP IN CANADA.

The High Commissioner for Canada in London has just received from the Dominion Bureau of Statistics at Ottawa, revised statistics dated July 23, on the production of metals on the platinum group in Canada.

The production of metals of the platinum group in Canada for 1922 was derived almost entirely from the nickel-copper ores of the Sudbury district. In accordance with the low production of nickel-copper, the amounts of metals of the platinum group recovered were comparatively small. The actual production figures have been augmented by the addition of quantities produced prior to 1922, but reported for the first time in that year.

The production was valued at the average New York quotations for the year, which were as follows: platinum \$97.618 per fine ounce, palladium \$65.00 per fine ounce, and osmium group \$80.00 per fine ounce.

METALS OF THE PLATINUM GROUP, CANADA, 1922.

	Platinum.	Palladium.	Rhodium, Osmium, Ruthenium & Iridium.
Produced by Canadian and United States nickel refineries from Canadian ores .....	fine ozs. 458	724	391
	Value \$ 44,709	\$ 47,060	\$ 331,280
B.C. Placers .....	fine ozs. 11	...	1
	Value \$ 1,074	...	80
Total for Canada .....	fine ozs. 469 (a)	724 (b)	392 (c)
	Value \$ 45,783	\$ 47,060	\$ 31,360

(a) includes—282 ounces platinum )  
 (b) includes—383 ounces palladium )  
 (c) includes—266 ounces of others )

GYPSUM.

The Dominion Bureau of Statistics, Canada, issues the finally revised statistics on the production of gypsum in Canada during 1922.

The total output of gypsum rock in Canada during 1922 amounted to 484,629 tons, of which quantity 145,954 tons, or 30 per cent., was calcined. The quantity quarried by provinces was: Nova Scotia, 281,861 tons; New Brunswick, 56,692 tons; Ontario, 106,829 tons; Manitoba, 39,147 tons; and British Columbia, 100 tons.

For statistical purposes the production of gypsum is considered to be the sum of the quantities disposed of in the different marketable forms, care being taken to avoid duplication; the values used are those at point of shipment.

Shipments of all grades totalled 559,265 tons, valued at \$2,160,898, an increase of 172,715 tons and \$375,360 over the 1921 production. The 1922 production included lump or mine run, crushed, fine ground and calcined gypsum sold; calcined gypsum used in the calcining plants for the production of wall plaster, alabastine and other gypsum products was also included. The average value per ton received by operators throughout Canada was, by grades: lump, \$1.52; crushed, \$2.26; fine ground \$6.22; and calcined, \$10.67. Prices during the previous year averaged as follows: lump, \$1.78; crushed, \$2.56; fine ground, \$3.42, and calcined, \$10.61.

The Dominion Bureau of Statistics has also issued finally revised statistics on the production of salt in Canada for last year.

The output of salt from all sources in Canada during 1922 totalled 183,438 tons,

Produced but not reported previous to 1922.

of which quantity approximately 99 per cent., or 181,794 tons, valued at \$1,628,323, was marketed. Compared with the sales for the previous year, the 1922 records showed an increase of 10,811 tons, or 6.6 per cent. in quantity, and a decrease of \$45,362 or 2.7 per cent. in value.

Ontario continued to be the chief producer, contributing 97.2 per cent. of the total sales. Nova Scotia shipments, from the Melagash Mine, amounted to 5,053 tons of common coarse, land and rock salt.

### BRITISH MALAYA.

#### CONSUMPTION OF ACETIC ACID.

With the exception of native rubber holdings and possibly of one or two large estates, all rubber latex produced in British Malaya is coagulated with acetic acid. During the war, when supplies of acetic acid were difficult to obtain, sulphuric acid came into general use. This acid is cheaper than acetic, but its use has been condemned by the Department of Agriculture of the Straits Settlements and Federated Malay States, and also by the Rubber Growers' Association.

The value of acetic acid imports has risen enormously since 1920. The sources from which the acid has been imported are interesting. In 1921 Canada furnished almost 50 per cent. of the supply, but by 1923 she has altogether ceased from competition in the market. The bulk of the acid is now supplied by European Continental countries. Details as to the respective quantities exported by the different countries of the Continent in 1922 and 1923 are not yet available, but in 1921 the Netherlands and Germany were the only two European Continental countries exporting the acid to Malaya. The value of Japanese acetic acid rose enormously in 1922, but has fallen again during the first half of the current year.

#### BOARD OF TRADE ANNOUNCEMENT. DYESTUFFS (IMPORT REGULATION) ACT, 1920. APPLICATIONS FOR LICENCE DURING AUGUST.

The total number of applications received during the month was 391, of which 269 were from merchants or importers. To these should be added the 29 cases outstanding on August 1, making a total for

the month of 420. These were dealt with as follows:—

Granted—282 (of which 248 were dealt with within seven days of receipt).

Referred to British makers of similar products—74 (of which 63 were dealt with within seven days of receipt).

Referred to Reparation supplies available—30 (all dealt with within two days of receipt).

Outstanding on August 31—34 (mostly dealt with at the meeting of the Committee held on August 31).

Of the total of 420 applications received, 341, or 81 per cent., were dealt with within seven days of receipt.

### APPEAL FOR BRITISH EMPIRE CANCER CAMPAIGN.

#### "HELP TO STAMP OUT CANCER!"

Following the announcement last week that the new Empire campaign against cancer was in need of voluntary workers, many offers of help have reached the headquarters of the British Red Cross Society, 19, Berkeley Street, W.1. The county branches of the Red Cross also report much enthusiasm amongst their workers who are enrolling thousands for active canvassing during the autumn campaign.

The example of Mr. Reuben Wood, of Sheffield, who recently lost his son through cancer, in collecting a sum of money for the campaign, a course he suggested to all who had lost relations or friends through this dreadful scourge, has been followed widely. Many requests have reached 19, Berkeley Street for books of stamps (of 1s. and 6d. denominations) to be sold for the benefit of the campaign, and for literature in the shape of leaflets and pamphlets describing the aims of the campaign. One enthusiastic young worker called on a recent morning at 19, Berkeley Street for a book of stamps valued at £1, and returned twice during the day for further supplies, having sold the others to his friends.

"Help to Stamp Out Cancer" is the slogan adopted for the cards of stamps which will be shortly on sale in many retail shops and other institutions. It is hoped that by the purchase of these stamps, which are of a striking design and may be affixed to correspondence, will afford the public an easy and convenient way of subscribing small amounts to this great cause.

Meantime larger subscriptions continue to be made to this fund, and it is hoped that the total sum required, £1,000,000, to subsidise and initiate further research throughout the Empire will eventually be secured.

Subscriptions should be sent to the Hon. Sir Arthur Stanley, G.B.E., C.B., M.V.O., British Empire Cancer Campaign Dept., British Red Cross Society, 19, Berkeley Street, W.1, or to any of the branches of Lloyds Bank, Ltd.

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### INSTITUTE OF METALS.

ANNUAL AUTUMN MEETING, HELD AT  
MANCHESTER, ON WEDNESDAY, SEPTEMBER  
12.

(Continued from Page 175.)

*The Constitution and Age-Hardening of the Quaternary Alloys of Aluminium, Copper, Magnesium and Magnesium Silicide*, by MARIE L. V. GAYLER, M.Sc.

The constitution and age-hardening of the quaternary alloys of aluminium, copper, magnesium, magnesium silicide, containing up to 6 per cent. copper, 4 per cent. magnesium, and 4 per cent. magnesium silicide, were considered.

In a quaternary system it is only possible to represent the equilibrium of the system at any single temperature, and the isothermal sections take the form of regular tetrahedra. For the above investigation isotherms at 400° C. and 250° C. have been determined from the results of thermal and microscopic examination, and wire models have been constructed.

The results show that when copper, magnesium, magnesium silicide are present in aluminium, any two of these components have a marked effect on the solubility of the third. The sum of these effects is that ultimately  $\text{CuAl}_2$  and  $\text{Mg}_2\text{Si}$  are both thrown out of solution. Also, if copper and magnesium are present in a ratio greater than 12 to 5 approximately, then alloys, when quenched from high temperatures, age-harden at room temperature, owing to the difference in the solubility of  $\text{Mg}_2\text{Si}$  at the quenching and ageing temperature. If, however, the ratio of copper to magnesium is less than 12 to 5, then no age-hardening takes place, since there is little difference in the solubility of  $\text{Mg}_2\text{Si}$

at high and low temperatures. The slight increase in hardness obtained on further heat-treating these quenched and aged alloys is attributed to the small difference in solubility of copper at the quenching and ageing temperature. It is shown, therefore, that the age-hardening of alloys of the "Duralumin" type is due primarily to  $\text{Mg}_2\text{Si}$ , copper causing very little age-hardening, and that the addition of magnesium and copper is important, since both reduce the solubility of  $\text{Mg}_2\text{Si}$  at high and low temperatures, and consequently reduce the maximum age-hardness due to  $\text{Mg}_2\text{Si}$ .

*The Electro-Chemical Character of Corrosion*, by ULICK R. EVANS, M.A.

Experiments have indicated that the corrosion of metals is mainly—probably entirely—electro-chemical in character. Corrosion accompanied by evolution of hydrogen gas is characteristic of reactive metals placed in acid solutions, but the velocity varies greatly with the purity of the metal. Where this type is impossible, slower corrosion can take place at a rate determined by the diffusion of oxygen to the metal, and comparatively independent of the purity. When a metal is immersed in a solution of potassium chloride, one can observe the production of alkali at the cathodic portions, the production of the chloride of the metal at the anodic portions, and the precipitation of hydroxide where these meet. The electric current can be trapped and measured, and is found (by applying Faraday's law) to account for the greater part of the corrosion actually observed. Generally the cathodic areas are those to which air has free access, whilst the anodic areas are those protected from aeration. It is significant that corrosion usually proceeds most rapidly at the comparatively "un-aerated" places—hence the intense corrosion observed in "pits" and over areas covered up by porous corrosion-products.

*Experiments with some Copper Wire; Cohesion a Function of both Temperature and Cold Work*, by DOUGLAS H. INGALL, M.Sc.

Five samples of copper wire were used, representing soft annealed and four degrees of cold work given by 25, 40, 50 and 75 per cent. reduction of area by drawing. Each sample of cold worked wire was obtained by drawing in one pass from the next thicker wire. The cohesion at elevated temperatures was determined by placing given loads

on the wire at atmospheric temperature, heating the wire and determining the temperature at which it broke. All the samples gave similar graphs (plotting cohesion against temperature) in which with rise of temperature the cohesion decreased along a straight line to a constant critical temperature of 350° C., beyond which the cohesion was represented by a sharply descending curve.

*Investigation of the Effects of Impurities on Copper. Part I.: The Effect of Oxygen on Copper*, by D. HANSON, D.Sc., C. B. MARRYAT, B.Sc., and GRACE W. FORD, B.Sc.

The effect of oxygen, up to a concentration of 0.36 per cent., on the properties of pure copper was described. The investigation deals with the casting of the metal, cold rolling, hot rolling, density of chill-castings and rolled bars, tensile tests at ordinary and at elevated temperatures, hardness tests, fatigue tests, notched-bar impact tests, electrical conductivity, microstructure of castings, and microstructures of the alloys in various conditions, and determination of the solubility of oxygen in solid copper.

The results indicate that oxygen has a relatively small effect on the properties of copper, and is neither seriously deleterious nor remarkably beneficial. The mechanical properties are not much affected by small quantities of oxygen, and copper containing as much as 0.1 per cent. differs very slightly from pure copper. The electrical conductivity, which is usually profoundly affected by the addition of small quantities of an impurity to a pure metal, does not fall rapidly, and values exceeding 100 per cent. of the International Standard are obtained in all annealed materials containing less than 0.1 per cent. of oxygen. The relatively small effect of oxygen is without doubt due to the fact that the solubility of the oxide in solid copper is extremely low, so low in fact that for all practical purposes oxygen may be regarded as insoluble in solid copper. The oxygen-bearing metals must, therefore, be considered as a heterogeneous mixture of pure copper and finely divided particles of cuprous oxide, and within the range of composition investigated the percentage of copper greatly exceeds that of cuprous oxide. The materials consist essentially of a soft ductile copper matrix, in which harder particles of cuprous oxide are distributed, and the properties of the series are such as would be expected

from a mechanical mixture of such constituents.

These conclusions, however, are applicable strictly only to pure copper containing oxygen and free from other impurities. The effect of the simultaneous presence of other impurities may be very appreciable, and requires special investigation, for which the present Report furnishes a necessary basis.

*Hardness Tests on Crystals of Aluminium*, by HUGH O'NEILL, M.MET.

In the Brinell hardness test the relation between the applied load ( $L$ ) and the diameter ( $d$ ) of the indentation produced on a specimen is given by  $L=ad^n$  (Mayer's formula). Many workers have determined the values of  $a$  and  $n$  for different metals, and the author has recently shown that for an amorphous substance  $n=2.0$ . The present work deals with completely crystalline material, single crystals of aluminium having been chosen since the technique of their production has been worked out by Professor Carpenter and Miss Elam.

Two pieces of aluminium strip were treated separately by their process, but only the first became a single crystal. By accident it was annealed for a short time just below its melting point and upon its upper surface three series of parallel ridged markings were visible. X-ray examination showed that this surface was a rhombic-dodecahedral (011) face, whilst two crystals chosen from the second piece proved likewise to be presenting octahedral (111) and cube (001) faces respectively.

Brinell tests showed that at low loads the different crystallographic planes resist penetration to different degrees, and give indentations of different shapes. In the Brinell sense the (110) face is the "hardest" and the cube (001) face appears to be the "softest." But the load required to immerse the ball—and probably eventually to make it perforate the metal—is apparently the same in all cases. Crystal boundaries were also found to be without any appreciable effect in increasing the resistance of aluminium to penetration. In terms of Meyer's formula, if a 1 mm. ball be used then whilst  $n$  varies from 2.483 for the (001) face to 2.274 for the (011) face,  $a$  is a constant for annealed aluminium. It is independent of the presence of grain boundaries and, in single crystals, of grain orientation.

*The Behaviour of Metals under Compressive Stresses*, by H. I. COE, M.Sc.

Compression tests carried out on small cylinders of metals show that with successive increments of loads plastic flow occurs, after the elastic limit has been exceeded, at an increasing rate. Graphical representation shows that at a certain load the rate of flow for a given increment of load undergoes a more or less abrupt change, very soft metals, such as tin and lead, becoming perfectly plastic, harder metals becoming more plastic than under preceding loads and immediately succeeding loads.

Annealed metals appear to commence flowing at a comparatively low load, and continue doing so at an increasing rate up to the load corresponding to critical plasticity; the same metals, however, in the worked condition are much more resistant to compressive stresses until they approach near the load corresponding to critical plasticity when they suddenly collapse and a marked temporary flow occurs.

*A Dilatometric Study of the Transformations and Thermal Treatment of Light Alloys of Aluminium*, by ALBERT M. PORTEVIN and PIERRE CHEVENARD.

Amongst the light alloys of aluminium capable of being hardened by quenching followed by tempering, is the group known under the name of Duralumin, whose essential characteristic is their magnesium content. The effect of the addition of this metal to aluminium was first pointed out by Wilm.

The investigations of Rosenhain, Archbutt, Hanson and Gayler have linked up the phenomena of quenching shown by these alloys, with the variation of the solubility, in solid aluminium, of  $Mg_2Si$ , which is always present in commercial aluminium. But the solubility curves of  $Mg_2Si$ , in solid aluminium, have only been indirectly traced by the examination of alloys quenched at different temperatures.

The authors conclude that (1) the application of dilatometric methods, judiciously using the recording differential dilatometer, permits of the study of the transformations and the mechanism of heat-treatment of the light alloys of aluminium-magnesium-silicon, and in general, of alloys containing two phase, univariant transformations, a study which had not been carried out up to the present. (2) The study of the constant temperature transformations by stant temperature transformations by the

differential dilatometer, using a high the differential dilatometer, using a high sensitivity apparatus, leads to general expressions representing the phenomena as functions of time and temperature. (3) The phenomena of quenching and tempering in the aluminium-magnesium-silicon alloys can be interpreted by the known variations in the solubility of  $Mg_2Si$  in the solid state, without it being necessary to assume any further transformations in these alloys.

*Equilibrium in the System Gold-Zinc* (based on Investigations of electrical conductivity at high temperatures), by PROF. P. SOLDAU.

Alloys of gold and zinc belong to the type of AR-brasses, where A is a metal belonging to the first, and R to the second group of the periodic system. These alloys are of considerable importance, as their chemical nature is very close to the alloys of copper with zinc, *i.e.*, to the ordinary brasses.

The system gold-zinc was investigated by R. Vogel in 1906, and no transformations were detected. However, the results of the investigation of the system gold-cadmium led the author to undertake the investigation of alloys of gold and zinc, taking advantage of several different methods of physico-chemical analyses, which would check and complement one another.

Special attention was paid to the determination of electrical conductivity at high temperatures, which necessitated the construction of a special apparatus.

When the results obtained by the electrical conductivity method at high temperatures and by quenching showed a complete concordance, then that former method could be recommended with sufficient guarantee for the investigation of other metallic systems, and in the first instance such practically important ones as those belonging to the type of brasses.

#### NOTICES OF BOOKS.

*Physikalische Chemie*, von DR. ALFRED BENRATH. Pp. VIII. + 107. Dresden & Leipzig: Verlag von Theodor Steinkopff. 1923. Price 2s.

Prof. Benrath's concise volume aims at being a monograph on the development of physical chemistry during the last decade.

He has divided his book into two parts. The first part, entitled *Chemically pure Bodies*, is very brief, occupying only 22 pages, and being concerned with the rela-

tions between elements and compounds and the theory of allotropy. A good account of the researches of the Dutch physicists on this subject is given.

Part II. deals with *Solutions*, and commences with remarks on Van't Hoff's Theory of Solution in the case of the solution of indifferent bodies. The case of Binary Mixtures is also described.

The solution of electrolytes receives fuller treatment, commencing with a description of the theory of electrolytic dissociation. Its position in 1914 and its subsequent development are traced, and an extensive bibliography is given. The theory of indicators and of completely dissociated electrolytes are discussed. There are also sections on the electrolytic dissociation of fused and of crystallised salts.

The development of the Solvate Theory of solutions is also traced, especially in connection with the question of the existence of hydrates in aqueous solutions.

In a small volume of this kind it is essential that a selection of the literature available must be made, and this has, in the main, been done with discrimination, but references to British work later than 1914 are inadequate. This is probably not the author's intention, but is a consequence of the inability of German scientists and institutions to purchase foreign publications.

At the low price of 2s., Prof. Benrath's book, which is Vol. VIII. of the *Naturwissenschaftliche Reihe*, published under the general editorship of Prof. Liesegang, should find a wide public among chemists and physicists, and especially advanced students, for whom it is evidently intended.

Messrs. David Bridge & Co., Ltd., Castleton, Manchester, have sent a copy of *Bridge's Modern Millgearing*, pp. 132. This work, which treats the subject more deeply than is usual in catalogues, contains many illustrations, diagrams, and working formulae, and an index. It is clearly printed on art paper, and prices for all classes of millgearing are quoted. There is also an appendix covering the field of power transmission, and should be of special interest to engineers and draughtsmen. A copy of the work may be obtained gratis on request.

#### BOOKS RECEIVED.

*Field Crops in South Africa*, by H. D. LEPPAN, B.Sc.A., and G. J. BOSMAN, B.Sc.A. Pp. IX. + 358. 1923. Central News Agency, Ltd., South Africa. 21s. net.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

202181—Coplan, A. H.—Production and refining of nickel-chrome steels.

*Abstract Published this Week.*

200175—Cleansing-compositions; sodium aluminium silicates.—Guernsey, F. H., of 7, Bewley Parkway, and Electric Smelting & Aluminium Co., both in Lockport, New York, U.S.A.

A crystalline detergent compound which is solid at ordinary temperatures, and having the formula  $Al_2O_3(SiO_2)_x(Na_2O)_{x-1}(H_2O)_y$ , where  $x$  represents any number greater than seven, is made by boiling together a mixture of aluminium silicate, sodium silicate, and caustic lye. The boiled mixture is preferably chilled to a semi-plastic condition, and allowed to solidify. When  $x$  has the value 75, the compound is completely soluble and has a melting-point of 126° F. To enhance the water-softening properties of the compound, alkali metal salts of weak acids such as sodium or potassium carbonates, or other carbonates, or phosphates or borates may be mixed with it. An emulsifying agent such as sulphonated or saponified oils or fats may also be added, preferably in amounts of about 5 per cent. To provide for loss of alkali oxide during cleansing operations, a further amount of oxide, up to 2 molecules for each molecule of detergent, may be mixed with the compound.

*Latest Patent Applications.*

21733—Badische Anilin & Soda-Fabrik.—Manufacture of oxygenated organic compounds. Aug. 28.

21659—Pellegrini, G.—Manufacture of meta-phenylene-diamine. Aug. 27.

21916—Pico, L.—Destructive fermentation of organic residues. Aug. 30.

22029—Scottish Dyes, Ltd.—Production of anthraquinone sulphonic acids. Aug. 31.

*Specifications Published this Week.*

202333—Mosicki, I.—Processes for the dry distillation of bituminous or cellulose containing material.

202383—Air Reduction Co., Inc.—Process of manufacture of alkali cyanides.

202,532—Germot, A.—Process for the direct obtaining of antimony.

*Abstract Published this Week.*

200739—Dyes, dyeing.—Chemische Fabrik Greisheim-Elektron, Frankfurt-on-Main, Germany.

*Monoazo dyes* are prepared in substance or on the fibre by coupling diazotized 5-nitro-2-toluidine with a *p*-alkyloxyarylide of 2:3-oxynaphthoic acid, the *p*-anisidide and *p*-phenetidine being mentioned; bluish-red, or in light tones, pink shades fast to light are thus obtained on the fibre; the products may also be used in the production of lakes. An example is given of the manufacture in substance of the dyestuff from 5-nitro-2-toluidine and the *p*-anisidide of 2:3-oxynitro-2-toluidine and the *p*-anisidide of 2:3-oxynaphthoic acid and of the production of pink and red shades on the fibre by padding with a solution containing the *p*-anisidide, caustic soda, turkey-red oil, and formaldehyde, and developing with the diazo compound.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.



## THE CHEMICAL NEWS,

VOL. CXXVII. No. 3311.

[BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE: LIVERPOOL, 1923.]

THE PRESIDENTIAL ADDRESS.  
THE ELECTRICAL STRUCTURE OF  
MATTER.BY PROFESSOR SIR ERNEST RUTHERFORD,  
D.Sc., LL.D., Ph.D., F.R.S.,*President of the Association.**(Continued from Page 182.)*

This artificial disintegration of elements by  $\alpha$  particles takes place only on a minute scale, and its observation has only been possible by the counting of individual swift hydrogen nuclei by the scintillations they produce in zinc sulphide.

These experiments suggest that the hydrogen nucleus or proton must be one of the fundamental units which build up a nucleus, and it seems highly probable that the helium nucleus is a secondary building unit composed of the very close union of four protons and two electrons. The view that the nuclei of all atoms are ultimately built up of protons of mass nearly one and of electrons has been strongly supported and extended by the study of *isotopes*. It was early observed that some of the radioactive elements which showed distinct radioactive properties were chemically so alike that it was impossible to effect their separation when mixed together. Similar elements of this kind were called 'isotopes' by Soddy, since they appeared to occupy the same place in the periodic table. For example, a number of radioactive elements in the uranium and thorium series have been found to have physical and chemical properties identical with those of ordinary lead, but yet to have atomic weights differing from ordinary lead, and also distinctive radioactive properties. The nuclear theory of the atom offers at once a simple interpretation of the relation between isotopic elements. Since the chemical properties of an element are controlled by its nuclear charge and little influenced by its mass, isotopes must correspond to atoms with the same nuclear charge but of different nuclear mass. Such a view also offers a simple explanation why

the radioactive isotopes show different radioactive properties, for it is to be anticipated that the stability of a nucleus will be much influenced by its mass and arrangement.

Our knowledge of isotopes has been widely extended in the last few years by Aston, who has devised an accurate direct method for showing the presence of isotopes in the ordinary elements. He has found that some of the elements are 'pure'—i.e., consist of atoms of identical mass—while others contain a mixture of two or more isotopes. In the case of the isotopic elements, the atomic mass, as ordinarily measured by the chemist, is a mean value depending on the atomic masses of the individual isotopes and their relative abundance. These investigations have not only shown clearly that the number of distinct species of atoms is much greater than was supposed, but have brought out a relation between the elements of great interest and importance. The atomic masses of the isotopes of most of the elements examined have been found, to an accuracy of about one in a thousand, to be whole numbers in terms of oxygen, 16. This indicates that the nuclei are ultimately built up of protons of mass very nearly one and of electrons. It is natural to suppose that this building unit is the hydrogen nucleus, but that its average mass in the complex nucleus is somewhat less than its mass in the free state owing to the close packing of the charged units in the nuclear structure. We have already seen that the helium nucleus of mass 4 is probably a unit of great importance in the building up of many atoms, and it may be that other simple combinations of protons and electrons of mass 2 and 3 occur in the nucleus, but these have not been observed in the free state.

While the mass of the majority of the isotopes are nearly whole numbers, certain cases have been observed by Aston where this rule is slightly departed from. Such variations in mass may ultimately prove of great importance in throwing light on the arrangement and closeness of packing of the protons and electrons, and for this reason it is to be hoped that it may soon prove possible to compare atomic masses of the elements with much greater precision even than at present.

While we may be confident that the proton and the electron are the ultimate units which take part in the building up of all

nuclei, and can deduce with some certainty the number of protons and electrons in the nuclei of all atoms, we have little, if any, information on the distribution of these units in the atom or on the nature of the forces that hold them in equilibrium. While it is known that the law of the inverse square holds for the electrical forces some distance from the nucleus, it seems certain that this law breaks down inside the nucleus. A detailed study of the collisions between  $\alpha$  particles and hydrogen atoms, where the nuclei approach very close to each other, shows that the forces between nuclei increase ultimately much more rapidly than is to be expected from the law of the inverse square, and it may be that new and unexpected forces may come into importance at the very small distances separating the protons and electrons in the nucleus. Until we gain more information on the nature and law of variation of the forces inside the nucleus, further progress on the detailed structure of the nucleus may be difficult. At the same time, there are still a number of hopeful directions in which an attack may be made on this most difficult of problems. A detailed study of the  $\gamma$  rays from radioactive bodies may be expected to yield information as to the motion of the electrons inside the nucleus, and it may be, as Ellis has suggested, that quantum laws are operative inside as well as outside the nucleus. From a study of the relative proportions of the elements in the earth's crust, Harkins has shown that elements of even atomic number are much more abundant than elements of odd number, suggesting a marked difference of stability in these two classes of elements. It seems probable that any process of stellar evolution must be intimately connected with the building up of complex nuclei from simpler ones, and its study may thus be expected to throw much light on the evolution of the elements.

The nucleus of a heavy atom is undoubtedly a very complicated system, and in a sense a world of its own, little, if at all, influenced by the ordinary physical and chemical agencies at our command. When we consider the mass of a nucleus compared with its volume it seems certain that its density is many billions of times that of our heaviest element. Yet, if we could form a magnified picture of the nucleus, we should expect that it would show a discontinuous structure, occupied but not filled by the

minute building units, the protons and electrons, in ceaseless rapid motion controlled by their mutual forces.

Before leaving this subject it is desirable to say a few words on the important question of the energy relations involved in the formation and disintegration of atomic nuclei, first opened up by the study of radioactivity. For example, it is well known that the total evolution of energy during the complete disintegration of one gramme of radium is many millions of times greater than in the complete combustion of an equal weight of coal. It is known that this energy is initially mostly emitted in the kinetic form of swift  $\alpha$  and  $\beta$  particles, and the energy of motion of these bodies is ultimately converted into heat when they are stopped by matter. Since it is believed that the radioactive elements were analogous in structure to the ordinary inactive elements the idea naturally arose that the atoms of all the elements contained a similar concentration of energy, which would be available for use if only some simple method could be discovered of promoting and controlling their disintegration. This possibility of obtaining new and cheap sources of energy for practical purposes was naturally an alluring prospect to the lay and scientific man alike. It is quite true that, if we were able to hasten the radioactive processes in uranium and thorium so that the whole cycle of their disintegration could be confined to a few days instead of being spread over thousands of millions of years, these elements would provide very convenient sources of energy on a sufficient scale to be of considerable practical importance. Unfortunately, although many experiments have been tried, there is no evidence that the rate of disintegration of these elements can be altered in the slightest degree by the most powerful laboratory agencies. With increase in our knowledge of atomic structure there has been a gradual change of our point of view on this important question, and there is by no means the same certainty to-day as a decade ago that the atoms of an element contain hidden stores of energy. It may be worth while to spend a few minutes in discussing the reason for this change in outlook. This can best be illustrated by considering an interesting analogy between the transformation of a radioactive nucleus and the changes in the electron arrangement of an ordinary atom. It is now well known

that it is possible by means of electron bombardment or by appropriate radiation to excite an atom in such a way that one of its superficial electrons is displaced from its ordinary stable position to another temporarily stable position further removed from the nucleus. This electron in course of time falls back into its old position, and its potential energy is converted into radiation in the process. There is some reason for believing that the electron has a definite average life in the displaced position, and that the chance of its return to its original position is governed by the laws of probability. In some respects an 'excited' atom of this kind is thus analogous to a radioactive atom, but of course the energy released in the disintegration of a nucleus is of an entirely different order of magnitude from the energy released by return of the electron in the excited atom. It may be that the elements, uranium and thorium, represent the sole survivals in the earth to-day of types of elements that were common in the long distant ages, when the atoms now composing the earth were in course of formation. A fraction of the atoms of uranium and thorium formed at that time has survived over the long interval on account of their very slow rate of transformation. It is thus possible to regard these atoms as having not yet completed the cycle of changes which the ordinary atoms have long since passed through, and that the atoms are still in the 'excited' state where the nuclear units have not yet arranged themselves in positions of ultimate equilibrium, but still have a surplus of energy which can only be released in the form of the characteristic radiation from active matter. On such a view, the presence of a store of energy ready for release is not a property of all atoms, but only of a special class of atoms like the radioactive atoms which have not yet reached the final state for equilibrium.

It may be urged that the artificial disintegration of certain elements by bombardment with swift  $\alpha$  particles gives definite evidence of a store of energy in some of the ordinary elements, for it is known that a few of the hydrogen nuclei, released from aluminium for example, are expelled with such swiftness that the particle has a greater individual energy than the  $\alpha$  particle which causes their liberation. Unfortunately, it is very difficult to give a definite

answer on this point until we know more of the details of this disintegration.

On the other hand, another method of attack on this question has become important during the last few years, based on the comparison of the relative masses of the elements. This new point of view can best be illustrated by a comparison of the atomic masses of hydrogen and helium. As we have seen, it seems very probable that helium is not an ultimate unit in the structure of nuclei, but it is a very close combination of four hydrogen nuclei and two electrons. The mass of the helium nucleus, 4.00 in terms of O=16, is considerably less than the mass 4.03 of four hydrogen nuclei. On modern views there is believed to be a very close connection between mass and energy, and this loss in mass in the synthesis of the helium nucleus from hydrogen nuclei indicates that a large amount of energy in the form of radiation has been released in the building of the helium nucleus from its components. It is easy to calculate from this loss of mass that the energy set free in forming one gramme of helium is large even compared with that liberated in the total disintegration of one gramme of radium. For example, calculation shows that the energy released in the formation of one pound of helium gas is equivalent to the energy emitted in the complete combustion of about eight thousand tons of pure carbon. It has been suggested by Eddington and Perrin that it is mainly to this source of energy that we must look to maintain the heat emission of the sun and hot stars over long periods of time. Calculations of the loss of heat from the sun show that this synthesis of helium need only take place slowly in order to maintain the present rate of radiation for periods of the order of one thousand million years. It must be acknowledged that these arguments are somewhat speculative in character, for no certain experimental evidence has yet been obtained that helium can be formed from hydrogen.

The evidence of the slow rate of stellar evolution, however, certainly indicates that the synthesis of helium, and perhaps other elements of higher atomic weight, may take place slowly in the interior of hot stars. While in the electric discharge through hydrogen at low pressure we can easily reproduce the conditions of the interior of the hottest star as far as regards the energy of

motion of the electrons and hydrogen nuclei, we cannot hope to reproduce that enormous density of radiation which must exist in the interior of a giant star. For this and other reasons it may be very difficult, or even impossible, to produce helium from hydrogen under laboratory conditions.

If this view of the great heat emission in the formation of helium be correct, it is clear that the helium nucleus is the most stable of all nuclei, for an amount of energy corresponding to three or four  $\alpha$  particles would be required to disrupt it into its components. In addition, since the mass of the proton in nuclei is nearly 1.000 instead of its mass 1.0072 in the free state, it follows that much more energy must be put into the atom than will be liberated by its disintegration into its ultimate units. At the same time, if we consider an atom of oxygen, which may be supposed to be built up of four helium nuclei as secondary units, the change of mass, if any, in its synthesis from already formed helium nuclei is so small that we cannot yet be certain whether there will be a gain or loss of energy by its disintegration into helium nuclei, but in any case we are certain that the magnitude of the energy will be much less than for the synthesis of helium from hydrogen. Our information on this subject of energy changes in the formation or disintegration of atoms in general is as yet too uncertain and speculative to give any decided opinion on future possibilities in this direction, but I have endeavoured to outline some of the main arguments which should be taken into account.

I must now bring to an end my survey, I am afraid all too brief and inadequate, of this great period of advance in physical science. In the short time at my disposal it has been impossible for me, even if I had the knowledge, to refer to the great advances made during the period under consideration in all branches of pure and applied science. I am well aware that in some departments the progress made may justly compare with that of my own subject. In these great additions to our knowledge of the structure of matter every civilised nation has taken on active part, but we may be justly proud that this country has made many fundamental contributions. With this country I must properly include our Dominions overseas, for they have not been behindhand in their contributions to this new knowledge. It is, I am sure, a matter of pride to this country

that the scientific men of our Dominions have been responsible for some of the most fundamental discoveries of this epoch, particularly in radioactivity.

This tide of advance was continuous from 1896, but there was an inevitable slackening during the War. It is a matter of good omen that, in the last few years, the old rate of progress has not only been maintained but even intensified, and there appears to be no obvious sign that this period of great advances has come to an end. There has never been a time when the enthusiasm of the scientific workers was greater, or when there was a more hopeful feeling that great advances were imminent. This feeling is no doubt in part due to the great improvement during this epoch of the technical methods of attack, for problems that at one time seemed unattackable are now seen to be likely to fall before the new methods. In the main, the epoch under consideration has been an age of experiment, where the experimenter has been the pioneer in the attack on new problems. At the same time, it has been also an age of bold ideas in theory, as the Quantum Theory and the Theory of Relativity so well illustrate.

I feel it is a great privilege to have witnessed this period, which may almost be termed the Renaissance of Physics. It has been of extraordinary intellectual interest to watch the gradual unfolding of new ideas and the ever-changing methods of attack on difficult problems. It has been of great interest, too, to note the comparative simplicity of the ideas that has ultimately emerged. For example, no one could have anticipated that the the general relation between the elements would prove to be of so simple a character as we now believe it to be. It is an illustration of the fact that Nature appears to work in a simple way, and that the more fundamental the problem often simpler are the conceptions needed for its explanation. The rapidity and certitude of the advance in this epoch have largely depended on the fact that it has been possible to devise experiments so that few variables were involved. For example, the study of the structure of the atom has been much facilitated by the possibility of examining the effects due to a single atom of matter, or, as in radioactivity of X-rays, of studying processes going on in the individual atom which were quite uninfluenced by external conditions.

In watching the rapidity of this tide of advance in physics I have become more and more impressed by the power of the scientific method of extending our knowledge of Nature. Experiment, directed by the disciplined imagination either of an individual, or still better, of a group of individuals of varied mental outlook, is able to achieve results which far transcend the imagination alone of the greatest natural philosopher. Experiment without imagination, or imagination without recourse to experiment, can accomplish little, but, for effective progress, a happy blend of these two powers is necessary. The unknown appears as a dense mist before the eyes of men. In penetrating this obscurity we cannot invoke the aid of supermen, but must depend on the combined efforts of a number of adequately trained ordinary men of scientific imagination. Each in his own special field of inquiry is enabled by the scientific method to penetrate a short distance, and his work reacts upon and influences the whole body of other workers. From time to time there arises an illuminating conception, based on accumulated knowledge, which lights up a large region and shows the connection between these individual efforts, so that a general advance follows. The attack begins anew on a wider front, and often with improved technical weapons. The conception which led to this advance often appears simple and obvious when once it has been put forward. This is a common experience, and the scientific man often feels a sense of disappointment that he himself had not foreseen a development which ultimately seems so clear and inevitable.

The intellectual interest due to the rapid growth of science to-day cannot fail to act as a stimulus to young men to join in scientific investigation. In every branch of science there are numerous problems of fundamental interest and importance which await solution. We may confidently predict an accelerated rate of progress of scientific discovery, beneficial to mankind certainly in a material but possibly even more so in an intellectual sense. In order to obtain the best results certain conditions must, however, be fulfilled. It is necessary that our universities and other specific institutions should be liberally supported, so as not only to be in a position to train adequately young investigators of promise, but

also to serve themselves as active centres of research. At the same time there must be a reasonable competence for those who have shown a capacity for original investigation. Not least, peace throughout the civilised world is as important for rapid scientific development as for general commercial prosperity. Indeed, science is truly international, and for progress in many directions the co-operation of nations is as essential as the co-operation of individuals. Science, no less than industry, desires a stability not yet achieved in world conditions.

There is an error far too prevalent to-day that science progresses by the demolition of former well-established theories. Such is very rarely the case. For example, it is often stated that Einstein's general theory of relativity has overthrown the work of Newton on gravitation. No statement could be farther from the truth. Their works, in fact, are hardly comparable, for they deal with different fields of thought. So far as the work of Einstein is relevant to that of Newton, it is simply a generalisation and broadening of its basis; in fact, a typical case of mathematical and physical development. In general, a great principle is not discarded but so modified that it rests on a broader and more stable basis.

It is clear that the splendid period of scientific activity which we have reviewed to-night owes much of its success and intellectual appeal to the labours of those great men in the past, who wisely laid the sure foundations on which the scientific worker builds to-day, or to quote from the words inscribed in the dome of the National Gallery, 'The works of those who have stood the test of ages have a claim to that respect and veneration to which no modern can pretend.'

[BRITISH ASSOCIATION, LIVERPOOL, 1923.]

SECTION I.—PHYSIOLOGY.  
SYMBIOSIS IN ANIMALS AND  
PLANTS.

ADDRESS BY GEORGE H. F. NUTTALL,  
M.D., PH.D., SC.D., F.R.S.

The address dealt with Symbiosis in Lichens, Root-nodules of Leguminous Plants, the significance of Mycorrhiza in various Plants, and Symbiosis in Animals.

The term "symbiosis" denotes a condi-

tion of conjoint life existing between different organisms that in a varying degree are benefited by the partnership. The term "symbiont," strictly speaking, applies equally to both the partners; it has, however, come to be used also in a restricted sense as meaning the microscopic member or members of the partnership in contradistinction to the physically larger partners which are conveniently termed the "hosts" in conformity with parasitological usage.

The condition of life defined as symbiosis may be regarded as balancing between two extremes—complete immunity and deadly infective disease. A condition of perfect symbiosis or balance is realised with comparative rarity because of the many difficulties of its establishment in organisms that are either capable of living independently or are incapable of resisting the invasion of organisms imperfectly adapted to communal life. In these respects the conclusions of Bernard and Magrou in relation to plants apply equally to animals. It is difficult to imagine that symbiosis originated otherwise than through a preliminary stage of parasitism on the part of one or other of the associated organisms, the conflict between them in the course of time ending in mutual adaptation. It is, indeed, probable that some supposed symbionts may prove to be parasites on further investigation.

In perfect symbiosis the associated organisms are completely adapted to a life in common. In parasitism the degree of adaptation varies greatly; it may approach symbiotic conditions on the one hand, or range to vanishing point on the other by leading to the death of the organism that is invaded by a highly pathogenic animal or vegetable disease agent. There is no definite boundary between symbiosis and parasitism. The factors governing immunity from symbionts or parasites are essentially the same.

No final conclusions can as yet be reached regarding the function of symbionts in many invertebrate animals owing to our ignorance of the physiological processes in the associated organisms. The investigation of these problems is one fraught with difficulties which we must hope will be surmounted.

New knowledge is continually being acquired, and a glance into new and even recent publications shows that symbionts have been repeatedly seen and interpreted as mitochondria or chromidia. The increasing number of infective diseases of animals

and plants, moreover, which have been traced, especially of recent years, to apparently ultramicroscopic organisms, cannot but suggest that there may exist ultramicroscopic symbionts.

We are on the threshold of further discoveries, and that a wide field of fruitful research is open to those who enter upon it. In closing, it seems—but fitting to express the hope that British workers may take a more active part in the elucidation of the interesting biological problems that lie before us in the study of symbiosis and the allied subject of parasitism.

[BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE. LIVERPOOL, 1923.]

SECTION A.—MATHEMATICS AND PHYSICS.

ON THE ORIGIN OF SPECTRA (RECENT PROGRESS).

ADDRESS BY PROFESSOR J. C. McLENNAN, F.R.S., PRESIDENT OF THE SECTION.

I.—INTRODUCTION.

The problem of the origin of spectra is intimately bound up with that of the constitution and structure of atoms. Models of atoms of different types have been proposed from time to time, and these all have served, in a measure, to explain some at least of the chemical, optical, and mechanical properties of matter. The conception, however, that inspires and co-ordinates the whole of modern atomic physics in so far as radiation is concerned is the remarkably simple atomic model of Rutherford and Bohr.

According to this model the neutral atom consists of a central positively charged nucleus with dimensions of the same order as those of the electron itself ( $10^{-13}$  cm.), and surrounded by a system of electrons whose aggregate negative charge is equal in amount to that of the positive charge carried by the nucleus. The *atomic number* gives for a neutral atom the number of electrons surrounding the nucleus, and is at the same time a measure of the positive electric charge carried by the latter.

Rutherford has shown that the electric field due to the charge on the nucleus is central, and that it follows the inverse square law practically up to the effective boundary of the nucleus. Close to the nu-

cleus the electric field is very intense, and therefore sufficient to produce those remarkably interesting deflections of alpha rays that are being studied so widely and so successfully at the present time by the use of C. T. R. Wilson's beautiful method of photographing cloud tracks.

With the introduction of the theory of *quanta* into the mechanics of the atom it became possible to analyse in detail the structure of atoms and to make quantitative comparisons between the properties of matter and those deducible from the different atomic models. In the developments that have taken place in this direction Niels Bohr has been the leader; but very notable and important contributions to the theory have been made by Wilson, Sommerfeld, Ehrenfest, Kramers, Lande, and others.

Bohr, in his theory, supposes that each electron in an atom describes a central or quasi-central orbit under the attraction of the nucleus in combination with the fields of the other extra-nuclear electrons present in the atom. He imposes, moreover, upon these motions of the electrons in atoms something in the nature of a quantum censorship.

From the continuous manifold of all conceivable states of motion that may be ascribed to an atomic system there exists a definable number of stationary states that possess a peculiar stability, and that are of such a kind that every permanent change of motion within the system must involve a complete transition from one stationary state to another.

It is postulated further that while no radiation is emitted by the atomic system when it is in one of its stationary states, the process of transition from one stationary state to another is accompanied by the emission of monochromatic radiation with a frequency given by the relation

$$\nu h = E_1 - E_2,$$

where  $h$  is Planck's constant and  $E_1$  and  $E_2$  are the values of the energy of the atom in the initial and final stationary states between which the transition takes place. Conversely, it is to be understood that the absorption by the atomic system of radiation with the frequency given above results in a transition back from the final stationary state to the initial one. These postulates, it will be seen, form the basis of an interpretation of the laws of series spectra, for the most general of these—the com-

bination principle of Ritz—asserts that the frequency  $\nu$  of each of the lines in the spectrum of a selected element can be represented by the formula

$$\nu = T_1 - T_2,$$

where  $T_1$  and  $T_2$  are two spectral terms taken from a number that are characteristic of the element in question.

On Bohr's theory the interpretation of the law of Ritz would be that the spectrum of the element referred to must originate in transitions between stationary states for which the atomic energy values are obtained simply by multiplying by Planck's constant the values of those spectral terms of which  $T_1$  and  $T_2$  are types.

This, it is evident, indicates the feasibility of establishing a connection between the series spectrum of an element and the constitution and structure of its atoms. From the spectrum of the element the series spectral terms can be selected and evaluated, and these values when multiplied by Planck's constant will give the various energy levels within and associated with the atom of the element. As the number of electrons within the said atom is given by the atomic number of the element, the problem becomes one of assigning to these constituent electrons orbits of a size and form that will provide the values of the energy levels determined by the spectral series terms.

The reciprocal nature of this relationship between the series spectrum of an element and its atomic structure will be evident. In a case where the series spectrum of an element is not known a knowledge of it may be obtained by determining the energy levels in the atoms of this element independently. This can be done after the manner of Moseley and Franck and Hertz by causing atoms to emit limited portions of its spectrum under bombardment by electrons of selected speeds.

#### STATIONARY STATES—QUANTUM CONDITIONS.

We may take the simple case of an atom of hydrogen which consists of a nucleus with charge  $+e$  and an electron with charge  $-e$ . The frequencies of the series spectra of this element are given with great accuracy by the Balmer formula

$$\nu = K \left( \frac{1}{n'^2} - \frac{1}{n''^2} \right) \quad (1)$$

where  $n''$  and  $n'$  are two integers and  $K$  is the Rydberg constant. All the spectral terms are of the form  $K/n^2$ , and the energy

corresponding to the various stationary states of the atom of hydrogen must be given by  $Kh/n^2$  with  $n$  having all possible integral values.

When an electron describes an elliptic orbit about the nucleus of a hydrogen atom the major axis of the orbit described is inversely proportional to  $w$  the work required completely to remove the electron from the field of the nucleus. The major axis is

given by  $2a = \frac{e^2}{w}$ . If, therefore, we take

$2a = \frac{e^2 n}{Kh}$  we have determined for the hy-

drogen atom a set of clearly defined stationary states consisting of a series of elliptical orbits for which the major axis takes on discrete values proportional to the squares of the whole numbers. Transitions from one to another of such a set of stationary states will suffice on Bohr's theory to account for all the lines in the series spectrum of atomic hydrogen.

Though the single principal quantum number suffices to define the energy levels for the atom of hydrogen, the introduction of the subordinate quantum numbers  $n_1$  and  $n_2$  extended the basis of the theory, and, as is well known, led to developments by Sommerfeld of profound importance in dealing with the question of the fine structure of spectral lines.

Bohr's theory of the origin of spectra as it exists to-day is approached from a somewhat different angle from that given above. Through extensions initiated independently by Wilson and by Sommerfeld the quantising conditions are made to apply to momentum rather than to energy, and in dealing with the problem of the *stationary states* of a system such as that of the hydrogen atom the angular and radial momenta of the electron in its orbit are both quantised.

#### QUANTUM NUMBERS AND THEIR SIGNIFICANCE.

For a given atomic system the quantum numbers define the stationary states, and the energy values and moments of momentum of the system in these states. Moreover, they define the kinematical character of the electron orbits in the atomic edifice, and on account of the simple relation connecting the values of spectral terms in the series spectrum of an element with the energy of the atom of this element in its various stationary states, they define these

spectral terms and enable us to calculate their values.

In the simplest possible treatment of a system such as that of the atom of hydrogen one quantum number  $n$  suffices to define the various factors just mentioned. In the theory of the fine structure of the spectral lines of hydrogen two quantum numbers  $n$  and  $k$  were required. In the case of a series spectrum of single lines two quantum numbers  $n$  and  $k$  are requisite to define its terms and the orbits corresponding to them. For a series spectrum consisting of doublets, triplets or multiplets, three quantum numbers are required,  $n$ ,  $k$  and  $j$ , to define its spectral terms and the corresponding electronic orbits. In the case of the resolution of a spectral line by the application of an external magnetic field a fourth quantum number  $m$  is necessary in order to distinguish the stationary states and to evaluate the spectral terms corresponding to the Zeeman components.

In spectroscopy it has become customary, in order to distinguish series of different kinds, to designate singlet systems by the use of capital letters, doublet series by Greek letters, and triplet series by small letters. Thus:

P S D F = singlet systems.

$\pi$   $\sigma$   $\delta$   $\zeta$  = doublet systems.

p s d f = triplet systems.

In the same way it has become customary to use the same letters to designate the spectral terms whose differences determine the frequencies of the lines in a series. As example we may cite 1S, 2S, &c.,  $1\pi$ ,  $2\pi$ , &c.;  $1d$ ,  $2d$ , &c.; and  $1f$ ,  $2f$ , &c.

#### PRINCIPLES OF SELECTION—THE CORRESPONDENCE PRINCIPLE.

In the early development of Bohr's theory it was found that the censorship imposed by the quantum conditions referred to above were not sufficiently drastic to account completely either for the observed complexity of the fine structure of spectral lines originating in the variation of the mass of an electron with its velocity or for the observed complexity and state of polarisation of the components of spectral lines that had their origin in the application of an external electric or magnetic field.

To make up for this deficiency arbitrary Principles of Selection, involving such factors as intensity and polarisation, were brought forward by Rubinowicz and by Sommerfeld, that found immediate and



remarkable verifications in the relativity fine structure of the Balmer lines, in the Stark effect, in the Zeeman effect, and in the spectra of rotation.

Although these principles of selection furnished rules that have served as useful guides in unravelling the intricacies of various types of spectral resolution, it has all along been recognised by the proposers, as well as by others, that the principles as formulated rested upon a dynamical basis that was rather limited and scarcely adequate.

The whole matter, however, was given an entirely new orientation and an enhanced significance by Bohr's enunciation of the Correspondence Principle.

The explicit hypothesis made by Bohr in his Correspondence Principle is that what has been shown above to be true necessarily for very great orbital periods is also sensibly true for finite ones as well. To put the matter in another way—if the orbit described by an electron were carried out under a law of action proportional to the distance, the development of the law of motion in a Fourier series would permit the use of a fundamental term only. The Correspondence Principle would under these conditions demand that the electron could pass spontaneously only from the  $n$ th quantum orbit to the  $n-1$  quantum orbit immediately below it. If these conditions were to apply in the case of the hydrogen atom, for example, it would limit each series to a single wave-length, and the Balmer series would be reduced to its first component.

The existence of series made up of numerous terms shows that the electronic orbits of an atom cannot be described under a central force varying as the direct distance, but points rather in the direction of the orbits being ellipses following approximately the Keplerian law.

In general, if the electronic motion within an atom is periodic and not simply of a pure sinusoidal character, Fourier's theory shows that the vibration of the electron is represented by a superposition of pure periodic motions that are harmonics of a fundamental one. To this classical notion there corresponds in the theory of quanta the notion of transitions from one stationary state to another with variations in the quantum number no longer equal to one only. If the Fourier series representing the motion contains effectively an harmonic of rank, 1, 2, 3 . . . or  $m$ , for ex-

ample, the Correspondence Principle postulates that the atom can be the seat of transitions corresponding to differences in the characterising quantum number of 1, 2, 3 . . . or  $m$ . If, on the contrary, the coefficient of a term in the Fourier series under consideration is small or equal to zero, this signifies that the probability of corresponding transitions in the atom becomes small or vanishes.

The Correspondence Principle co-ordinates every transition process between two stationary states with a corresponding harmonic vibration component in such a way that the probability of the occurrence of the transition is dependent on the amplitude of this particular vibration.

#### THE GENESIS OF ATOMS.

One of the more interesting of the recent developments of Bohr's theory is that which concerns the genesis of atoms of different types. Bohr has put forward the view that the fundamental process that must apply consists in the successive binding of electrons one after another by a nucleus originally naked.

On this view the electrons as they are successively bound to the nucleus take up certain final and definite orbits that are characteristic of the particular atom selected in its *normal* state, and that can to a first approximation be specified by two quantum numbers—namely, the principal and subordinate quantum numbers  $n$  and  $k$ . This means that the motion of each single electron of the atomic system can be approximately described as a plane periodic motion on which is superimposed a uniform rotation in the plane of the orbit.

It is assumed as a general postulate that during the binding of an electron by a nucleus the values of the quantum numbers  $n$  and  $k$  that characterise the orbits of the earlier bound electrons remain unchanged, and that at most, apart from a few exceptional cases, the addition of the later bound electrons merely results in slight alterations in the orientations in space of the orbits of the electrons already bound.

#### THE FINE STRUCTURE OF THE BALMER LINES OF HYDROGEN.

In the simplest treatment by the quantum theory of the origin of the spectrum of atomic hydrogen no allowance is made for a variation in the mass of the electron with its speed. If this factor be taken into account, as it has been by Sommerfeld, it is found that the motion of the electron is

reducible to a motion in an elliptic orbit upon which is imposed a slow rotation in its own plane about the nucleus as focus. The resulting orbit has the form of a rosette, and is similar to that shown in Fig. 5.

In this treatment the chief factor in determining the stationary states is the principal quantum number  $n$ , but the subordinate quantum number  $k$  is also contributory. The former practically determines the major axis and the period of the elliptical orbit, while the latter defines the parameter of the ellipse—*i.e.*, the shortest chord through its focus. The subordinate quantum number  $k$  also determines the period of rotation of the elliptic orbit in its plane. The energy corresponding to each stationary state is in the main determined by the value of the quantum number  $n$ , but stationary states determined by the same value of  $n$  are characterised by energy values that vary slightly with different values of the quantum number  $k$ .

#### MODEL OF THE ATOM OF HELIUM.

From the chemical point of view, helium is considered to be inert. Of all atoms it is the most stable, for it has the highest ionisation potential, namely, 24.5 volts. A study of the X-radiation emitted by the elements generally makes it appear that the configuration we assign to the electronic orbits in helium atoms is maintained intact throughout the whole of the remaining heavier elements. These orbits, as already shown, constitute for all atoms the K X-ray group the innermost and most stable system. For these reasons it is highly desirable that a model of the atom of helium be realised possessing high stability endowed with the capacity to emit radiation exhibiting the characteristic features of the helium spectrum, and having energy values for its normal and temporary stationary states that fit in with the experimentally determined values of its ionisation, resonance, and other critical excitation potentials.

#### THE KOSSEL-SOMMERFELD DISPLACEMENT LAW.

In arriving at his scheme of atomic orbits, Bohr was guided by the view that the fundamental process to keep in mind was that when a nucleus originally naked acquired electrons sufficient in number to neutralise its charge, it did so by binding them according to a programme that was definite and fixed for each value of the nuclear charge.

(To be continued.)

## ORGANIC MERCURY COMPOUNDS.

### PART I.

By R. F. HUNTER, F.C.S.

Some few days ago a short review was given of our present knowledge of organic arsenic compounds, with particular reference to their immense value in dealing with protozoal diseases, mainly in reference to their use in venereal work. This leads to the consideration of organic mercury compounds owing to the fact that it has become customary in recent years to use non-ionised mercury compounds in conjunction with aromatic arsenicals, such as salvarsan. In view of this, no apology is called for in connection with this article, which is intended only as the roughest of outlines on a subject which has been attracting the attention of some of our leading researchers for many years.

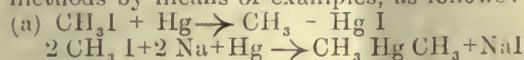
The study of organic compounds of mercury carries us back to the year 1843, when A. W. von Hofmann, later professor of chemistry at the Royal College of Science, discovered a mercury compound which he prepared from aniline and mercuric chloride, and to this day the nature of the aforesaid compound, prepared as above, is a matter for discussion. Seven years later, Frankland discovered the reaction between alkyl halides and mercury. Four years after this Stricker prepared ethyl mercuric iodide.

In 1868 mercury dinaphthyl was discovered, followed the next year by Wurtz's discovery of mercury diphenyl. Subsequently Reynolds, Cahours, Meyer and Michaelis studied various compounds and preparations. 1892 saw the publication of Pesci's researches on mercury derivatives of aromatic amino compounds (aniline), researches of immense importance. In 1894 researches on the preparation of mercury derivatives of phenol and corresponding naphthalene compounds were published by Desesquelle, and three years later Bamberger discovered his reaction between  $N_2O_3$  and the diphenyl of mercury. Dimroth the following year showed that mercuration of aromatics is a process of nitration or sulphonation.

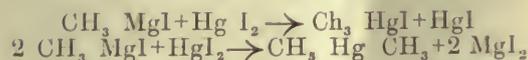
Of more recent date, we have had such researches as Pesci's action between mercuric acetate and phthalic acid, published in 1901, the application of Grignard's reaction to organic mercury compounds by Pfeiffer, 1904, the study of mercury derivatives of

nitrophenol by Hantrich in 1908. The long and academic researches of Schoeller and Schrauth started in the same year as Hantrich's results, and in 1913 the electrolysis of solutions of alkyl mercuric halides in liquid ammonia.

It will be advisable to mention the chief methods of preparation of organic mercury compounds. We can enumerate the methods by means of examples, as follows:

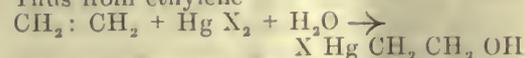


Sodium Amalgam

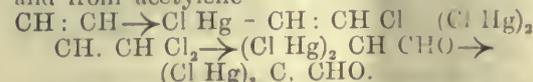


(b) Preparation by means of mercuric oxides, for instance, if one treats alcohol with mercuric oxide and sodium hydrate, ethane hexamer carbide,  $C_2Hg_6 O_4H_2$ , is produced, in which we have hydrogen atoms of methyl groups replaced by mercury atoms. Similar compounds can be obtained from the action of mercuric oxide on aldehydes and ketones.

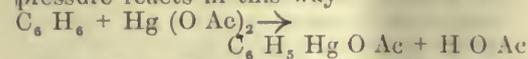
(c) A third method of preparation is to treat unsaturated compounds with mercuric salts in aqueous or alcoholic solution. Thus from ethylene



and from acetylene

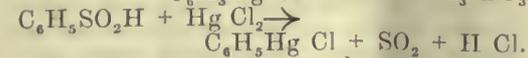
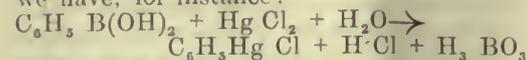


(d) A fruitful reaction has been that of the direct action of mercuric acetate on aromatic compounds. Thus benzene under pressure reacts in this way



Certain phenyl 5 pyrazolones have also been mercurated by this method, some three or four mercury atoms being introduced, some of which go into benzene nucleus and some of which go into the pyrazolone ring.

(e) The last reaction we shall mention is the action of mercuric chloride solution on aromatic borie and sulfinic acids, when we have, for instance:



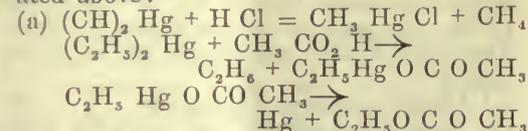
Before proceeding to study some of the mercury compounds, it will be advisable to pay some attention to the general properties and reactions. Whitmore, in his "Organic

Compounds of Mercury," classified the reactions under the headings of

- (a) Action of acids.
- (b) Action of bases.
- (c) Action of sulphides.
- (d) Change of compounds of type  $R Hg X$  to  $R_2 Hg$ .
- (e) The reverse change of  $R_2 Hg$  to  $R Hg X$ .
- (f) Action of halogens.
- (g) Action of halides and cyanides of metals.
- (h) Action of halides of non-metals.
- (i) Action of alkyl and aryl halides.
- (j) Action of acid halides.
- (k) Action of metals.

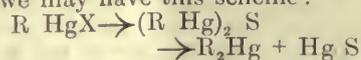
Before proceeding to examples of these, there is one point necessary to be noted, and that is: the linkage of mercury to carbon is capable of far greater stability than that of any other metal.

For instance, a compound  $CH_3 Hg I$ , unlike the corresponding magnesium compound, is not acted upon by water, amines and alcohols. Also organic mercury halides do not react with compounds containing carbonyl. Further, the mercury in organic compounds reacts differently from ionised mercury, and the organic mercury halides can give double decomposition reactions in the same way as inorganic halides. We now consider the typical reactions under Dr. Whitmore's classification, as enumerated above:



(b) Many compounds dissolve in solutions of the bases, and are recovered unchanged by allowing to cool, also bases do not normally break the carbon mercury linkage. Compounds having a free phenol or  $CO_2 H$  group are soluble in bases. Many mercury compounds of these types readily yield anhydrides, or rather inner salts, which are insoluble in water. These compounds dissolve in alkalis yielding solutions of corresponding salts.

(c) The reactions of organic mercury compounds with sulphides vary greatly. Thus we may have this scheme:



Certain compounds, such as alkyl mercuric iodide, react instantly with sulphides. It has been noticed that the compounds which react most readily are those in which the mercury atom is alpha w. carboxyl or phenyl, this giving the alpha atom its high reactivity.

The beta compounds react very slowly, if at all, and in most cases do not react at all.

Thus hydroxy mercury methyl malonic ester is unacted upon by ammonium sulphide.

(d) Change from  $R Hg X$  to  $R Hg R$ .

We usually have to carry out the change in presence of a reagent; we can represent it as



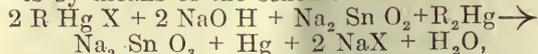
The  $\alpha$  thiophene mercuric iodides undergo the change without the addition of reagents. If we treat the chloride with  $NaI$  in the usual way, a quantity of mercury dithionyl crystallises out, and the iodide is left in the mother liquors.

The iodides which change to  $R_2Hg$  compounds on heating are  $\alpha$  thiophene mercuric iodide and  $\alpha$  iodo  $\alpha$  iodo mercuric thiophene. When dealing with substituted anilides the action of an excess of alcoholic  $NaI$  is the best method for preparing  $R_2Hg$  compound, thus *o*. acetoxy mercuri *p*. bromodimethylaniline yields quantities of mercury diphenyl on refluxing some eight hours with potassium iodide or sodium iodide. A point of interest is the formation of a mercury di  $\beta$  phenylanthro hydroacrylic acid from anhydro  $\alpha$  hydroxy mercuric  $\beta$  methoxy hydrocinnamic acid and potassium iodide.

The most general method for producing  $R_2Hg$  compound from  $R Hg X$  compounds is by the sodium thio sulphate method. The reaction has been made use of in the case of

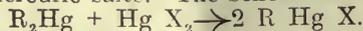
- (1) Phenyl mercury compounds.
- (2) Substituted aniline and toluidine mercury compounds.
- (3) Mercury compounds of diphenylamine.
- (4) Phenol mercury compounds.
- (5) Aminobenzoic acid mercury derivatives.
- (6) Salicylic ester mercury derivatives.

Another method of obtaining the change is by means of the scheme:



which has been applied to such cases as ethyl mercuri chloride diepi iodhydrine dimercuric bromide. Mercurated nitro and dinitro benzoic acid, and others.

(e) Reaction between  $R_2Hg$  compounds and mercuric salts. The scheme is:



This reaction has been carried out with such compounds as

- Mercury dimethyl;
- „ diethyl;
- „ di isoamyl;
- „ di cyclohexyl;

Cyclomercuri pentamethylene;

Mercury diphenyl;

„ di benzyl;

„ di anilines;

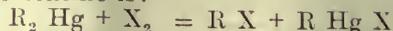
„ di anisoles;

„ di phenetoles;

„ di thionyl compounds.

(f) Reaction with halogens.

The scheme is:



The reaction carried out in such cases as mercury dimethyl.

Mercury di *n* propyl;

„ di isobutyl;

„ di isoamyl;

„ di octyl;

also with Iodonethylmercuric iodide.

Chloromethyl mercuric iodide;

Diethyl ether dimercuric iodide;

Di epi iodohydrine di mercuric iodide;

$\beta$  Acetoxy mercuriethyl methyl ether.

Mercury bis mono chloroacetylene reacts with iodine in ethereal solution to give chlorotri iodoethylene.

Mercury bis tri chloroethylene reacts with chlorine to give perchloroethane and  $Hg Cl_2$ . Anhydro hydroxy mercuri nitro acetic ester reacts with bromine to give dibromo nitro acetic ester.

Mercury diazo acetic ester with iodine gives an explosive organic compound.

The reaction has also been applied in cases of

Penta methylene di mercuric iodide;

Penta methylene di mercuri phenyl;

Tolyl mercuric chlorides;

Monomercurated phenols;

Mercurated nitro phenols;

Mercurated benzoic acid;

Mercurated Salicylic acid.

Acetoxy mercuric phenyl glycine ethyl ester.

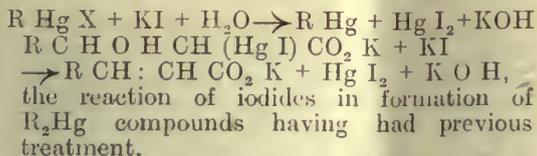
Mercurated quaternary ammonium compounds.

Mercurated anthranilic acid and mercury dinaphthyl.

Mercurated  $\beta$  naphthol carboxylic acid. Also mercurated camphor in benzene solution of iodine gives di iodo camphor, which can be converted into a quinone of camphor.

Cineol mercuric iodide reacts with iodide in ether to give a liquid iodide, which we believe to be cineol iodide, but where composition has yet to be proved.

(g) The reactions with halides and cyanides of metals are indicated by the scheme:



The reactions above are clearly those of Hg - C linkage splitting.

K C N has the effect of splitting many C - Hg linkages which are unaffected by K I, for instance, ethanol mercuric compounds react with K C N yielding  $C_2H_4$  on warming.

Tetra acetoxy mercuri di acetone hydrate reacts with K C N to give acetone.

(h) The reaction with non-metallic halides is worthy of mention.

$B Cl_3$ , for instance, reacts giving mercuric halides and compounds of type  $R B Cl_2$ .

$P Cl_3$  reacts with mercury dimethyl, yielding methyl mercuric chloride.

$As Cl_3$  reacts with mercury dipropyl to give tri propylarsine, thionyl chloride reacts with mercury aromatic compounds, giving corresponding aromatic mercuric chloride.

(i) The reaction with alkyl and aryl halides is not of very great importance.

Examples are:

Methylene di mercuric chloride reacts with  $C_2H_5I$  to give methyl mercuric iodide at  $140^\circ$ .

Mercury diphenyl heated at  $200^\circ$  with  $C_2H_4Br_2$  gives phenyl mercuric bromide.

(j) The reaction with acid halides is likewise not very important. We might mention that mercury compounds containing amine or hydroxyl groups can be acetylated without affecting the mercury, and that the mercury addition products of ethylene compounds are capable of benzoylation.

(k) The reaction with metals is well known, for instance, sodium reacts with mercury, dimethyl and diethyl, to give corresponding sodium compounds.

The methods of preparation and the general properties and reactions of the organic mercury compounds having been given a brief review, it is proposed to now study some of the more important typical compounds in some detail, following more or less the system of Whitmore, which appears to be the best at the present time.

## GENERAL NOTES.

### STORES REQUIRED FOR THE NETHERLANDS COLONIAL GOVERNMENT SERVICE.

Mr. R. V. Laming, O.B.E., Commercial Secretary at The Hague, reports that the Kolonial Etablissement, 2, Westerdoksdijk, Amsterdam, is inviting tenders to be presented by 1 o'clock on September 19 for the supply and delivery of various goods, including 700 K.G. dyestuff, ultramarine; 50 K.G. dyestuff, "Kogelblauw" (wash blue); 7,000 K.G. carbonate of soda; 8,000 K.G. yellow soap.

The conditions of tenders and deliveries are contained in the "Algemeene Bepalingen betreffende de aanschaffing van goederen ten behoeve van 's Lands dienst in de Koloniën," a copy of which is in the possession of the British Chamber of Commerce for the Netherlands East Indies, Abbey House, 1, Victoria Street, London, S.W.1, who have expressed their willingness to allow interested British firms to consult it.

Copies of the specifications (in Dutch), which also contain the special conditions of tender, may be consulted by British firms on application to the Enquiry Room, Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.

The possession of a representative in Holland is an essential condition of tendering, and British firms not locally represented should apply to the Department of Overseas Trade for the names of likely agents to act for them in this matter.

### CZECHO-SLOVAKIA'S FOREIGN TRADE IN JULY.

The Officer in Charge for the Commercial Secretary at Prague informs the Department of Overseas Trade that, according to the official figures just published by the State Office of Statistics, the value of the Czecho-Slovak exports for July amounted to 1,008 million crowns, and the imports to 744 million crowns, thus showing a balance of 264 million crowns in favour of exports. The exports for the first seven months of this year totalled 6,621 million crowns, and the imports 4,816 millions, an excess of 1,704 million of crowns of exports over imports.

### AUSTRALIA'S FOREIGN TRADE FOR THE YEAR ENDED 30 JUNE, 1923.

Mr. S. W. B. McGregor, H.M. Senior Trade Commissioner in Australia, has informed the Department of Overseas Trade that the statistics of Australian trade for the year ending 30 June, 1923, show that the imports were £131,808,673, as compared with £127,846,535 for the previous year, a decrease of £9,923,452.

The balance of trade favourable to Australia in 1921-22, amounting to £24,780,099, has become an adverse balance of £13,895,590 in 1922-23.

The accumulation of Australian funds in London, together with new loan money, has had a stimulating effect on imports and some reaction, temporarily unfavourable to British trade, must be expected.

The decrease in the value of exports in 1922-23 is largely due to the fall in the value of wheat, which accounts for £20,136,000 of the decrease as compared with 1921-22. The increase in the value of wool exported was £9,163,000.

There has been a marked increase in the value of imported manufactured apparel and in textiles generally, the total for this class being £44,914,128 compared with £34,149,710 in 1921-22. Some falling off in these lines of trade must now be anticipated.

The total value of imports of metals, metal manufactures, and machinery was £35,195,931, compared with £25,096,571 in 1921-22, of which chassis for motor cars are valued at £6,117,179, compared with £2,927,759 in the previous year. This extraordinary increase in the value of the imports of motor cars is an indication of the prosperity of Australia generally, and a growing feeling that a motor car is a necessity for the efficient conduct of town or country avocations.

Information as to countries of origin and destination of imports and exports respectively will not be available for several months.

### NOTICES OF BOOKS.

*Redwood and Eastlake's Petroleum Technologist's Pocket-Book*, Revised by A. W. EASTLAKE, M.I.MIN.E., A.M.I.-MECH.E. Pp. 546. Second Edition. London: Charles Griffin & Co., Ltd., Exeter Street, Strand, W.C.2. 1923. Price 15s.

The need for a small handy work of reference on petroleum has been met by the publication, in 1915, of this pocket-book. Its proved usefulness has led to the appearance of a second and revised edition by Mr. Eastlake, to which Sir Thomas H. Holland, Vice-President of the Institution of Petroleum Technologists, etc., has contributed a Foreword.

Chemists and technologists may be reminded that the volume contains much condensed information concerning the Geology, Physics, and Chemistry of Petroleum. A good deal of space is devoted to production, which is followed by a section on refining, transport, storage and testing. In addition to statistical tables, weights and measures, there is also a miscellaneous section, which gives a list of the Courses of Instruction in Petroleum Technology in various centres; an inclusive list of petroleum periodicals; Passport Regulations; Numerals, etc., in eight languages; etc.

Eight small but useful maps, indicating the sources of petroleum and other deposits, are contained in a pocket at the end.

The extent of the revision of this edition may be gauged by the fact that over 100 pages have been added, but the bulk of the book is the same, since it is printed on thinner (but very good) paper.

The book reflects credit upon all concerned with its publication, and should prove to be of especial value to petroleum technologists.

*The Phase Rule and the Study of Heterogeneous Equilibria. An Introductory Study*, by A. C. D. RIVETT, M.A., D.Sc. Pp. 204. Oxford: At the Clarendon Press. Price 10s. 6d. net.

The theoretical importance of the Phase Rule is not likely to be under-estimated so long as the work of Professor Ostwald is remembered. But the Phase Rule is not only important from the theoretical point of view. As Professor Rivett writes: "The study of heterogeneous equilibria, from the standpoint of the Phase Rule and the Principle of Le Chatelier and Braun, is one which every manufacturer would do well to require from his chemical staff. Whether or not costly evaporations are necessary, or recrystallisations, or extractions with

solvents, only systematic work will show. The cost of such investigation will usually be slight compared with the gains that will be made possible." In view of these facts, the small number of text-books dealing with the subject of the Phase Rule that are available seems to be totally incommensurate with the importance of the subject, and a very hearty welcome is therefore extended to this introductory study by Professor Rivett, which it is hoped will tend to stimulate further interest therein.

The work is strictly in the nature of an introduction, and, as the author points out, must not be regarded as constituting either a treatise or a book of reference; which fact, perhaps, explains the absence of an index. The author's aim has been to discuss types of systems which may be met, and ways in which such systems may be graphically represented, and to giving some examples of the manner in which conclusions of practical importance may be deduced.

The author commences his treatment of the graphical representation of various systems by means of three dimensioned models, from which the more usual two dimensioned graphs are obtained by considering special planes. This is, as he points out, not the usual procedure, but, although students may have some little difficulty in dealing with the three dimensioned models, the method certainly has the advantage of being more logical than the more customary one. In fact, the logical quality of Dr. Rivett's treatment throughout calls for favourable notice. In the Preface, for example, he calls attention to the fact that when we are dealing with mixtures containing more than one component there cannot be equilibrium between two phases unless each component is present in each phase. As concerns solid phases, this fact is (except in special cases) usually ignored, owing to the very small solvent power of solids. Unless, however, the formation of solid solutions is recognised, the subject cannot be presented in such a way that conclusions shall strictly conform throughout to the basic principles summarised in the Phase Rule.

In dealing with mixtures of three components, considerable use is made of Gibb's equilateral triangle diagrams. There is also a long chapter dealing with four component systems, and another containing some simple thermo-dynamical considerations relevant to the subject.

H. S. REDGROVE.

*Rhus Dermatitis (Poison Ivy) — Its Pathology and Chemotherapy*, by JAMES B. McNAIR. Pp. IX. + 298. The University of Chicago Press, 5750, Ellis Avenue, Chicago, Illinois, U.S.A. \$4.00 (post paid \$4.15).

Of all cutaneous eruptions caused accidentally by plant substances, that resulting from the poison oak or poison ivy is the most common in North America. The lack of any rational treatment for this common poisoning has led Mr. McNair into a protracted study of the isolated principle, in the hope that knowledge of its characteristic properties may serve as a basis for such treatment.

From a general botanical description of the plants, *Rhus Toxicodendron*, *R. radicans*, and especially *R. diversiloba*, which have long been known under the names of poison ivy or poison oak, it is shown that the fresh sap emulsion from the resin canals alone is dangerous. All other parts of the plant have been shown to be non-toxic. The poisonous properties also decrease as the fruit ripens.

The author has traced the chemical investigations into the nature of the poisonous principle — lobinol — which has been shown to contain only carbon, hydrogen, and oxygen, and which is a phenolic compound. An exact knowledge of its chemical nature is of supreme importance if a rational remedy for its action is to be sought. The substance was originally regarded as a volatile alkaloid, and later as an acid until the absence of any carboxyl group was proved. Consequently the early remedies adopted were quite empirical.

The volume contains much interesting matter relating to pathological cases, immunity, and the chemo-therapy of the subject, and concludes with a comprehensive bibliography of botanical, chemical and pathological references.

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We have received a copy of the *Announcements* of the Northampton Polytechnic Institute, giving particulars of the courses of instruction in the different branches of Scientific and Engineering Industries.

On this occasion the new issue deals with the evening work only. The well-known work dealt with in the day section of the *Announcements* will be practically the same as last session, there being only small changes in details of syllabuses which can be made as the work develops.

The whole of the work includes day and evening courses in Engineering (Civil, Mechanical and Electrical), in Optical Engineering and Applied Optics, and in Horology. The Engineering courses include sub-sections in Automobile work, Aeronautics, and Radio-Telegraphy. In addition there are evening courses in Electro-Chemistry, Metallurgy, and Domestic Economy and Women's Trades. The classes for the day courses commence on Monday, October 1, and those for the evening courses on Monday, September 24. Enrolments for the latter commenced on Monday, the 17th inst.

Full details of the syllabuses and the equipment are also given.

#### PUBLICATIONS RECEIVED.

The U.S. Department of the Interior, Bureau of Mines, has just issued the following pamphlets:

*Explosives—Their Materials, Constitution and Analysis*, by C. A. TAYLOR and WM. H. RINKENBACH. Pp. XI. + 188.

*Progress of Investigations on Liquid-Oxygen Explosives*, by S. P. HOWELL, J. W. PAUL and J. L. SHERRICK. Pp. VII. + 91.

*Anhydrous Aluminium Chloride*, by OLIVER C. RALSTON. Pp. IV. + 38.

*Fires in Steamship Bunker and Cargo Coal*, by H. H. STOEK. Pp. IV. + 51.

*The Motor Gasoline Surveys of 1920 and 1921* (A sequel to Bulletin 191), by N. A. C. SMITH. Pp. 41.

*Mine Rescue Standards—A Tentative Study*, prepared by a Committee appointed at the International Mine Rescue Standardisation Conference, September, 1921. Pp. IV. + 43.

*Permissible Explosives, Mining Equipment and Apparatus approved prior to January 1, 1923*, by S. P. HOWELL, L. C. ILSLEY, D. J. PARKER and A. C. FIELDNER. Pp. 22.

*Sodium Sulphate: Its Sources and Uses*, by ROGER C. WELLS. Pp. IV. + 43.

*Geology and Ore Deposits of the Creede District, Colorado*, by WM. H. EMMONS and ESPER S. LARSEN. Pp. IX. + 198.

*The Commercial Granites of New England*, by T. NELSON DALE. Pp. XV. + 488.

*The Kotsina-Kuskulana District, Alaska*, by FRED H. MOFFIT and J. B. MERTIE, JR. Pp. VII. + 149.

*Ilsemanite at Ouray, Utah*, by FRANK L. HESS. Pp. 16.

*Mineral Resources of the United States, 1920—Part I.*

*Mineral Resources of the United States in 1920—Introduction*, by G. F. LOUGHLIN. Pp. 155a.

*Coke and By-Products in 1921*, by R. S. McBRIDE. Pp. 444.

*Peat in 1922*, by K. W. COTTRELL. Pp. 6.

*Surface Waters of Wyoming and Their Utilisation*, by ROBERT FOLLANSBEE. Pp. X. + 331.

*Geology and Ground-water Resources of Sacramento Valley, California*, by KIRK BRYAN. Pp. XI. + 285.

*The Industrial Utility of Public Water Supplied in the United States*, by W. D. COLLINS. Pp. 59.

*Comparative Tests of By-Product Coke and Other Fuels for House-Heating Boilers*, by HENRY KREISINGER, JOHN BLIZARD, H. W. JARRETT and J. J. MCKITTERICK. Pp. 21.

*Tests of Low-Grade and Complex Ores in Colorado*, by WILL H. COGHILL and C. O. ANDERSON. Pp. 67.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

22166—Beckett, E. G.—Production of anthraquinone derivatives. Sept. 3.

22625—Helbronner, A.—Manufacture of chromates, etc. Sept. 8.

22429—Keller, A.—Manufacture of sulphuric acid. Sept. 6.

22447—Tokalon, Ltd.—Manufacture of oleo stearate or glyceryl. Sept. 6.

#### Specifications Published this Week.

175987—Silica Gel Corporation.—Process of recovering liquid solutes from non-aqueous solutions.

202664—Saltrick, W. A.—Manufacture of iron-chromium alloys.

*Alkali thiosulphates, carbonates, and sulphocyanides.*—Liquors containing alkali thiosulphates and other less soluble alkali salts such as carbonates, which may be products of gas-purifying processes such as those described in Specifications 169,996 and 170,572, are evaporated until the boiling point reaches 120° C. at atmospheric pressure, when the salts such as alkali carbonates separate, and the crystals are removed in a centrifugal apparatus. The solution is then cooled to obtain crystals of thiosulphate. The mother liquor may be further concentrated to obtain a second crop of thiosulphate crystals; the final mother liquor contains sulphocyanides. The thiosulphate crystals are washed and recrystallised, the mother liquor being returned to the evaporator.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3312.

[BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE: LIVERPOOL, 1923.]

## SECTION B—CHEMISTRY. SOME ASPECTS OF THE PHYSICAL CHEMISTRY OF INTERFACES.

By PROFESSOR F. G. DONNAN, C.B.E.,  
F.R.S., PRESIDENT OF THE SECTION.

It was at the last meeting at Liverpool, in 1896, that I first had the honour of attending a gathering of the British Association. On that occasion Dr. Ludwig Mond, F.R.S., was President of Section B, and I shall never forget the interest and pleasure I felt in listening to the Address of that great master of science and scientific method. Little did I dream that in 1923 I should have the honour and privilege of occupying the Chair of Section B at Liverpool.

Looking back on the Liverpool Meeting of 1896, one can say now that it came at the dawn of a new era in the development of physico-chemical science. The X-rays had just been discovered by Röntgen. Perin had proved experimentally (1895) that a negative electric charge was associated with the cathode rays and had surmised that these so-called "rays" were constituted by electricity in motion, thus corroborating Crookes' brilliant views of a decade earlier and demonstrating that Lenard was wrong. Sir J. J. Thomson had just begun that splendid series of researches which resulted not only in the complete elucidation of the nature of the cathode "rays," but also in the discovery of the negative electron as a constant, universal, and fundamental constituent of all matter.

The discovery of the chemically inert elementary gases by Raleigh and Ramsay had begun in 1894, and the series of investigations which finally led to the recognition of the radio-active transformations of atoms and to the discovery of the nature and constitution of the atom itself, were just beginning. During the last twenty-five years the influence of these discoveries on chemical science has been enormous. There has come about a fresh reunion of physics and chemistry, somewhat analogous to that which occurred in the days of Volta and

Davy. During the two decades preceding 1896, physical science had been largely concerned with the phenomena of the "ether," with electric and magnetic fields, electromagnetic waves, and the identification of light and other forms of radiant energy as electromagnetic phenomena. Now that the physicists have brought physical science back to the close and intimate study of matter, physics and chemistry have come together again, and the old and homogeneous science of "natural philosophy" has been reconstituted. It is time that the walls which divide our chemical and physical laboratories were broken down, and that the young men and women who come to our Universities to study physics or chemistry, should study the facts and principles of a fundamental science which includes both.

In recent years a great deal of attention has been paid to the phenomena which occur at the surfaces or interfaces which separate different sorts of matter in bulk. During the last quarter of the nineteenth century, both J. Willard Gibbs and J. J. Thomson had shown the peculiar nature of these interfacial or transitional layers. Things could happen in these regions which did not occur in the more homogeneous and uniform regions well inside the volume of matter in bulk. Such happenings might, if they could be investigated, reveal molecular or atomic peculiarities which would be undetectable in the jostling throng of individuals inside. A surface or surface layer represents a sort of thin cross section which can be probed and examined much more readily than any part of the inside bulk. It is indeed only within comparatively recent years that the X-rays have provided a sufficiently fine probe for examining this bulk in the case of crystalline matter.

In the theories of Laplace, Gauss, and Poisson, the field of force surrounding an attracting element or molecule was regarded as essentially uniform in its spatial relations, *i.e.*, the equipotential surfaces were regarded as concentric spheres with the molecule as a small element at the centre. The molecules were thought of as possessing what one might call a very rounded and somewhat monotonous "physical" character as regards their fields of force. In recent years our views have undergone a radical transformation. The field force surrounding a molecule may be very "irregular," and specially localised

around certain active or "polar" groups. Its region of sensible magnitude may be very variable and relatively small compared with molecular dimensions. The chemical constitution of the molecule is now regarded as determining the varying nature of the field of force surrounding it, so that parts of the molecule possessing high "residual chemical affinity" give rise to specially powerful regions of force. In this way the older "physical" theories of cohesion according to central forces with uniform orientation have been to some extent replaced, or at all events supplemented, by "chemical" theories according to which the attractive force-fields are highly localised round active chemical groups and atoms, are relatively minute in range, and can be saturated or "neutralised" by the atoms or groups of neighbouring or juxtaposed molecules.

Dr. W. B. Hardy has been the chief pioneer in the development of these newer theories, having been led thereto by his researches on surface tension, surface films, composite liquid surfaces and static friction and lubrication.

His ideas are clearly expressed in the following: "If the field force about a molecule be not symmetrical, that is to say, if the equipotential surfaces do not form spheres about the centre of mass, the arrangement of the molecules of a pure fluid must be different at the surface from the purely random distribution which obtains on the average in the interior. The inwardly directed attractive force along the normal to the surface will orientate the molecules there. The surface film must therefore have a characteristic molecular architecture, and the condition of minimal potential involves two terms—one relating to the variation in density, the other to the orientation of the fields of force." (1913.)

These conclusions have been confirmed by W. D. Harkins, who has found that in the case of very many organic liquids the "adhesion work" towards water is greatly increased by the presence of oxygen atoms (as in alcohols, acids, and aldehydes). The very symmetrical halogen derivatives,  $\text{CCl}_4$  and  $\text{C}_2\text{H}_4\text{Br}_2$ , give markedly low values for their adhesion work towards water, and that in the case of unsymmetrical molecules, the adhesion work towards water is determined by the presence of certain active atoms or atomic groups.

The question of the orientation of molecules at the surfaces of liquids has been greatly extended by a study of the extreme-

ly thin and invisible films formed by the primary spreading of oily substances on the surface of water. In a continuation and development of the work of Miss Pockels, the late Lord Rayleigh showed many years ago that when olive oil forms one of these invisible films on water, there is no fall in surface tension until the surface concentration reaches a certain very small value. He made the highly interesting and important suggestion that this concentration marks the point where there is formed a continuous layer just one molecule thick. This work was repeated and extended by H. Devaux and A. Marcelin, who showed the correctness of his suggestion that the primary film consists of a *unimolecular* layer. It appears, however, that the fall in surface tension which he ascribed to the building up of a bimolecular layer, is due to the closer packing of the molecules of the unimolecular layer.

Let us now consider another type of formation of surface layers at the surfaces of liquids—namely, the case where a substance dissolved in a liquid concentrates preferentially at the liquid-air or liquid-vapour interface. Gibbs, and later J. J. Thomson, have shown that if a dissolved substance (in relatively dilute solution) lowers the surface tension, it will concentrate at the surface. That such a phenomenon actually occurs has been qualitatively demonstrated in the experiments of D. H. Hall, J. von Zawidzki, and F. B. Kenrick and C. Benson, by the analysis of foams and froths. In 1908 S. R. Milner used the same method in the case of aqueous solutions of sodium oleate, and arrived at a mean value of  $1.2 \times 10^{-10}$  gram mols. excess concentration per sq. cm. of surface. Now, in the case of dilute solution, we can calculate  $q$ , the amount concentrated or "adsorbed" in the surface per sq. cm. (excess surface concentration) by making use of the equation of Gibbs,

$$q = - \frac{d\gamma}{d\mu}$$

where  $\gamma$  = surface tension and  $\mu$  = chemical potential of the adsorbed substance in the bulk of the solution. Writing  $\mu = RT \log a + k$ , where  $a$  = "activity" of the solute, and  $k$  is a quantity dependent only on the temperature and nature of the solute and solvent,  $d\mu = RT d \log a$ , and so Gibbs' equation can be written in the form

$$q = - \frac{1}{RT} \frac{d\gamma}{d \log a}$$

If for very dilute solutions (or "ideal" solutions) we can write

$$q = \frac{1}{RT} \frac{d\gamma}{d \log c} = \frac{c}{RT} \frac{d\gamma}{dc}$$

In this way Milner has calculated from Whatmough's data for aqueous solutions of acetic acid that the "saturation" value of  $q$  is  $3.3 \times 10^{-10}$  mols. per sq. cm., from which it follows that the area per molecule in the surface is  $50 \times 10^{-16}$  sq. cm. In a similar manner, Langmuir has calculated from B. de Szyszkowski's data for aqueous solutions of propionic, butyric, valeric, and caproic acids that the surface area per molecule adsorbed in the saturated layer is equal to  $31 \times 10^{-16}$  sq. cm., whilst Harkins has arrived from his own measurements for butyric acid at the value  $36 \times 10^{-16}$  sq. cm.

In 1911 Dr. J. T. Barker and myself made a direct determination of  $q$  for a solution of nonylic acid in water. For a practically saturated surface layer it was found that  $q$  was about  $1.0 \times 10^{-7}$  grm. per sq. cm., or  $3.1 \times 10^{14}$  molecules per sq. cm. From this result it follows that the surface area per molecule is  $26 \times 10^{-16}$  sq. cm.

If we consider these various values, it will be at once evident that they are not very different from the values found by Langmuir and by Adam for the oriented unimolecular layers of practically insoluble fatty acids resting on the surface of water. That in the present case some of the values are larger might easily be explained on the ground that these adsorption layers are partially, or completely, in the state of "surface vapours." For Adam and Marcellin have recently made the important discovery that the unimolecular surface films investigated by them may pass rapidly on increase of temperature from the state of "solid" or "liquid" surface films to the state of "vaporised" surface films, in which the juxtaposed molecules become detached from each other and move about with a Brownian or quasi-molecular motion, probably communicated to them by the thermal agitation of the water molecules to which they are attached.

It is, indeed, highly probable that the molecules which are concentrated in the surface from the state of solution in the liquid phase are not in quite the same situation as the molecules of practically insoluble substances which are placed on the surface. In the former case the molecules are still "dissolved," so that they will be more subject to thermal agitation and less

able to form a juxtaposed unimolecular layer. They may also be "hydrated." The difference between the two cases is rendered very evident from the fact that in the production of surface layers from dissolved molecules of the fatty acids (and other "surface active" substances) there is a very marked fall of surface tension, whilst the uncompressed unimolecular surface films placed on the surface from outside do not affect the surface tension of the water. Thus the molecules of the surface-active substance in the former case are in much closer relation to the solvent molecules, and are in kinetic equilibrium with the molecules of both solvent and solute in the bulk of the liquid. Nevertheless, the agreement as regards order of magnitude in the values of the surface area per molecule in the two types of case is certainly very suggestive and significant. Moreover, the experiments of Mr. Iredale show that molecules which are adsorbed on the surface from the vapour phase lower the surface tension, and are therefore from this point of view comparable with molecules concentrated in the surface from the bulk of the liquid phase.

The question as to whether the simplified form of Gibbs' equation yields a sufficiently accurate value for the excess surface concentration can scarcely be decided without more experimental data. In the experiments made by Dr. Barker and myself, the values calculated from the surface tension-concentration curve were  $1.3 \times 10^{-7}$  and  $0.6 \times 10^{-7}$  grm. per sq. cm., according as the value of the van't Hoff factor  $i$  for the very dilute solutions of nonylic acid was taken as 1 or 2 respectively; whilst the corresponding directly determined value was about  $1.0 \times 10^{-7}$  grm. per sq. cm. This discrepancy was probably well within the experimental error of our measurements.

Within the last few years H. A. McTaggart has made a number of experiments on the electric cataphoresis of gas bubbles in aqueous solutions and other liquids. He finds that aliphatic acids and alcohols in aqueous solution reduce the surface P.D., and that this effect runs parallel with their influence on the surface tension of water. He also finds that acids reduce the P.D. These results may be regarded as a corroboration of those obtained by Kenrick. McTaggart has found that the nitrates of tri- and tetravalent cations have a powerful effect in not only reducing but reversing the P.D. (i.e., the bubble becomes positively

charged). His experiments also show that polyvalent negative ions, such as the ferrocyanide ion, act in the opposite direction to the polyvalent cations—i.e., they increase the negative charge on the bubble or diminish a previously existing positive one. These results are of great interest, inasmuch as they show the powerful effects produced by polyvalent ions on the P.D. existing in the surface layer of an aqueous solution. As we shall see presently, very similar results have been obtained at liquid-liquid and solid-liquid interfaces. But it is of great importance to know what happens at the air-liquid interface, since we can largely discount the chemical and physical influence of the gas phase.

Although the electrometric method employed by Kenrick and Thorwaldson only gives comparative results (since two interfaces must always be simultaneously used), whilst the cataphoresis method gives results for a single interface, it is necessary to observe that the electrometric method measures the *total* fall of potential from the bulk of one phase to the bulk of another. The cataphoresis method measures what Freundlich has called the "electrokinetic" P.D.—that is to say, the potential drop between the limiting surface of the "fixed" part of the double layer and the rest of the liquid. The two values need not necessarily coincide.

Let us now inquire how far the phenomena which we have seen to be characteristic of a gas-liquid interface occur also at the interface between two immiscible or partially miscible liquids. Many years ago it was shown by Gad and by Quincke that a fatty oil is very readily dispersed in the form of an emulsion by a dilute solution of caustic soda. A neutral hydrocarbon oil can be similarly emulsified in a dilute aqueous solution of alkali if one of the higher fatty acids was dissolved in it, whilst the lower fatty acids do not produce a similar action. It was shown that the action runs parallel to the lowering of interfacial tension and must be ascribed to the formation of a soap, which lowers the interfacial tension and concentrates at the interface.

I cannot conclude this account of certain aspects of surface actions and properties without making a passing, though all too brief, reference to the beautiful investigations of Sir George Beilby on the amorphous layer. He has shown that when the surface of crystalline matter is subjected to shearing stress, there is produced a surface

layer of a vitreous or amorphous character—a "flowed" surface—in which the particular ordered arrangement of the molecules or atoms which is characteristic of the crystalline matter largely disappears. Dr. Travers and Mr. R. C. Ray have recently obtained a very interesting confirmation of the Beilby Effect. The heats of solution (in kilogram calories per gram mol) of vitreous silica and silver sand (silica as crystalline quartz) in aqueous hydrofluoric acid were found to be 37.24 and 30.29 respectively. After grinding for fifteen hours the corresponding values were 36.95 and 32.46 respectively. If we assume that the internal energy of the amorphous phase produced by grinding is the same as that of the vitreous silica (silica glass), we can calculate from these results that about 31 per cent. of the crystalline silica has been converted by grinding into "amorphous" silica. The densities of silica glass and silver sand were found to be 2.208 and 2.638 respectively. After fifteen hours' grinding the density of the latter was lowered to 2.528. On the same assumption as before, it follows that about 26 per cent. of the quartz has been converted into the vitreous condition. The difference between the figures 31 and 26 is doubtless due to the approximate character of the assumption underlying the calculations and to experimental errors. There seems little doubt, however, about the soundness of the main conclusion—namely, that the mechanical action of shearing stress on crystalline matter is to produce a random molecular or atomic distribution in the surface layers.

This discussion, necessarily brief and limited, of certain aspects of the properties of surfaces—molecular orientation, surface concentration or adsorption, electrical or ionic polarisation—has dealt very largely with states of thermodynamic equilibrium.

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#### SECTION, A.—MATHEMATICS AND PHYSICS.

#### ON THE ORIGIN OF SPECTRA (RECENT PROGRESS).

ADDRESS BY PROFESSOR J. C. McLENNAN, F.R.S., PRESIDENT OF THE SECTION.

(Continued from Page 202.)

If this view be accepted, it follows that if we were to detach from the neutral atom of

an element its most loosely bound electron, we should expect to find that the orbits which remained were characterised by the same quantum numbers as defined them in the neutral atom. Moreover, except in certain special cases, these orbits would be identical in type with those of the neutral atoms of the next lighter element. The exceptional cases would include those elements whose atomic structure involved the commencement of the development of an inner system of orbits, such as those of the  $3_3$ ,  $4_3$ ,  $4_4$ , &c., groups. Subject to these limitations, we should expect to find that if the  $n$  last-bound electrons were removed from a neutral atom of an element the orbits that remained in this atom would be identical in type with those of the neutral atoms of the  $n$ th lighter element. This would mean that the arc spectrum of the monovalent positive ion of an element would be identical as to types of series involved with the arc spectrum of the neutral atoms of the next lighter element. There would be this difference, however, that in the series formulæ of the spectrum of the ion the Rydberg constant would be  $4K$ , whereas in the series of the spectrum of the neutral atoms of the lighter element it would be  $K$ . Putting the matter as it is ordinarily stated, the spark spectrum of an element should be made up of series of the same type as those of the arc spectrum of the next lighter element. This is known as the Kossel-Sommerfeld Displacement Law.

In terms of Bohr's theory the 9-fold value of the Rydberg constant would be interpreted as meaning that aluminium atoms which emitted this spectrum had lost two electrons, and were represented by  $Al^{+++}$ , or, as it is now written,  $Al(III)$ . The 16-fold Rydberg constant would, on the same theory, also be interpreted as meaning that the atoms of silicon which emitted this spectrum were those that had lost three electrons, i.e.,  $Si(IV)$ . These results, it will be seen, amply confirm the view that the bound electrons in the neutral atoms of sodium  $Na(I)$ , are of the same type and are characterised by the same quantum numbers as those of the singly ionised atom of magnesium,  $Mg(II)$ , of the doubly-ionised atom of aluminium,  $Al(III)$ , and of the trebly-ionised atom of silicon,  $Si(IV)$ .

What has been found to be true of the spectra of sodium, magnesium, aluminium, and silicon, will no doubt be found to be true of the spectra elements lithium, beryllium, boron, and carbon. The spectra of beryllium and boron are extremely meagre

in wave-lengths, and but little is known of their spectral series. The spectrum of carbon, however, especially in the extreme ultra-violet, has been well worked out by a number of observers, and particularly so by Simeon.

In the spectrum of beryllium the doublet  $\lambda = 3131.194 \text{ \AA}$ ,  $\lambda = 3130.546 \text{ \AA}$ , has been shown to be the first member of a principal and a second subordinate series of doublets. Moreover, Back, who recently investigated its magnetic resolution, has found that the magnetic components are of the  $D_1$  and  $D_2$  type, just as Kent has shown the magnetic components of the close lithium doublet  $\lambda = 6708 \text{ \AA}$  to be. It will, therefore, probably be found when the spectrum of beryllium has been extended that the doublet  $\lambda = 3131.194 \text{ \AA}$ ,  $\lambda = 3130.546 \text{ \AA}$ , will prove to be the first member of the doublet series of the positive singly-charged atom of beryllium, with a Rydberg constant for the series of  $4K$ . In the spectrum of boron the doublets  $\lambda = 2497.73 \text{ \AA}$ ,  $\lambda = 2496.78 \text{ \AA}$ , and  $\lambda = 2089.49 \text{ \AA}$ ,  $\lambda = 2088.84 \text{ \AA}$ , particularly the latter, merit attention in looking for a  $9K$  series. In the ultra-violet spectrum of carbon there is a strong doublet at  $\lambda = 1335.66 \text{ \AA}$ ,  $\lambda = 1334.44 \text{ \AA}$ , and another nearly as strong at  $\lambda = 1329.60 \text{ \AA}$ ,  $\lambda = 1329.07 \text{ \AA}$ . These two also merit attention in any attempt to identify  $16K$  series for this element.

In considering the general validity of the Kossel-Sommerfeld Displacement Law the recent work of Catalan on the series spectra of manganese, chromium and molybdenum is of interest.

In this paper an attempt has been made to outline some of the leading features of the quantum theory as it is being used to solve the problems of atomic structure as well as of those connected with the origin of radiations emitted by atoms. Other illustrations of special interest might have been drawn from the treatment of problems that have arisen in a study of band spectra and of fluorescence phenomena. The recent work of Cabrera, Epstein, and Dauvillier, on paramagnetism, too, has a most interesting connection with the development of inner systems of electronic orbits in atoms in Bohr's scheme of the genesis of atoms.

I venture to think, however, that the few illustrations presented may serve, in a measure, to indicate the power and also the beauty of the methods being put forward to elucidate the problem of the origin of radiation.

## ORGANIC MERCURY COMPOUNDS.

## PART II.

BY R. F. HUNTER, F.C.S.

*(Continued from Page 205.)*

Mercury dimethyl is the first alkyl mercury compound we shall consider.

It can be prepared in several ways, for instance, by the action of sodium amalgam on methyl iodide, from zinc dimethyl and methyl mercuric iodide, from methyl mercuric iodide and potassium cyanide, from mercuric chloride and ether methyl magnesium iodide or aluminium carbide. It is a colourless, highly refractive and excessively poisonous liquid, and reacts with halogens, acids, metals, iodic cyanogen, stannous chloride, phosphorus and antimony trichloride, with potassium permanganate and with mercuric salts.

The important synthetical compound methyl mercuric acetate is prepared from it by heating it with glacial acetic acid in a sealed tube for some time at 130°; methane is produced in this reaction.

The homologue, mercury diethyl, is prepared by similar methods, *e.g.*, from zinc diethyl and mercuric chloride, from ethyl bromide and sodium amalgam, from ethyl mercuric iodide and potassium cyanide, etc. It reacts in a similar manner with halogens, metals, acids, potassium permanganate, mercuric salts, etc., with arsenobenzene, on heating at 150°, a reaction takes place in which phenyl diethyl arsine is formed and metallic mercury produced.

Among the other alkyl mercury compounds which have been prepared, we might mention: mercury dipropyl, diisobutyl, di sec. butyl, di isoamyl, di octyl, the preparations of which can be found in Whitmore's excellent book on the subject.

A number of mercury compounds have been prepared from the olefines. For instance, ethylene reacts with aqueous solutions of mercuric salts, giving a variety of complex mercury compounds. These have been classified as:

Ethanol mercuric salts;

Ethyl ether mercuric salts;

and products of the form  $C_2H_3Hg(OR)X$ .

As derivatives of ethylene we might mention Ethanol mercuric chloride, bromide and iodide; Ethanol mercuric nitrate and sulphide;  $\beta\beta'$  di chloro mercuric diethyl ether; Mercurous and mercuric diethylene oxides.

Certain products obtained from ethylene and alcoholic solutions of mercuric salts, such as  $\alpha$  Acetoxymercuri,  $\beta$  methoxy ethane, and  $\alpha$  Acetoxy mercuri  $\beta$  ethoxy ethane. Mercury compounds have also been prepared from propylene, for instance,  $\alpha$  Acetoxymercuri  $\beta$  hydroxypropane, and from isobutylene: chloromercuri hydroxy isobutane.

The mercury compounds of acetylene are of interest from the synthetical production of acetaldehyde from acetylene in the presence of salts of mercury. We might mention mercury bis mono chloro acetylene as an acetylene derivative of particular interest.

Ethyl alcohol in the presence of alkali reacts with mercuric salts producing a variety of compounds, of which the most important are the mercarbides, which are compounds in which the hydrogen of a  $CH_3$  group is completely replaced by mercury. Ethane hexamercarbide,  $C_2Hg_6O_2(OH)_2$ , is typical, and is produced by the refluxing of yellow  $HgO$ ,  $KOH$ , and alcohol for several hours.

The dichloride and corresponding nitrate and sulphate of ethane hexamercarbide have been prepared.

Mercury compounds of unsaturated alcohol, such as vinyl, allyl alcohols, have been prepared, and quite a large amount of research has been carried out on the action of mercuric salts on allyl alcohol.

The mercury derivatives of the fatty acids, aldehydes, ketones, and acid amides have been subject to much investigation. A variety of compounds are prepared from carbon monoxide and alcoholic solutions of mercuric salts. We might mention acetoxy mercuri formic methyl ester and the corresponding ethyl compounds as examples. Among the mercurated acetic acids we have

Bromo mercuri acetic acid;

Anhydro hydroxy mercuri acetic acid;

Nitrate mercuri acetic acid;

Mercuri nitrate mercuri acetic acid;

Dichloromercuri acetic acid;

Trichloromercuri acetic acid; and

Tri hydroxy mercuri acetic acid.

Among the mercurated propionic acids, we have  $\beta$  mercury bis propionic acid and its corresponding anhydride, and the anhydride of a hydroxy mercuri propionic acid.

Compounds from unsaturated acids have also been prepared such as the anhydride of  $\alpha$  hydroxy mercuri,  $\beta$  hydroxy propionic acid, and the anhydride of hydroxy mercuri  $\alpha$  hydroxy  $\beta$  butyric acid.

The mercury salts of  $\alpha$  acetoxy mercuri  $\beta$  hydroxy mercuri and  $\beta$  hydroxy methyl succinic acid have been prepared.

As examples of mercury aldehyde compounds we have

Mercuri chlorate, mercuri aldehyde, mercuri nitric, mercuri acetaldehyde.

A variety of compounds are obtained when acetone reacts with mercury compounds. We might state

Tetra acetoxy mercuri diacetone hydrate; and

Tri mercuri diacetone hydrate as examples.

Mercury acetamide,  $(\text{CH}_3 \text{C O N H})_2 \text{Hg}$ , is typical of the mercury derivatives of acid amides, and is prepared by adding yellow  $\text{HgO}$  to melted acetamide and allowing the temperature to rise slowly to  $180^\circ$ . Among the other amide derivatives which have been prepared by various workers at different times, we might mention

Mercury monochloro acetamide;

„ nitro acetamide;

„ propionamide;

„ oxamide;

„ succinamide;

„ tartamide and fumaramide.

The mercury derivatives of aromatic hydrocarbons and nitro compounds have been dealt with fully by Whitmore, and hence nothing more than the briefest of reviews will be given.

A typical example is mercury diphenyl, which can be prepared by several methods:

1.—By action of sodium amalgam on  $\text{C}_6\text{H}_5\text{Br}$ .

2.—From  $\text{C}_6\text{H}_5\text{Br}$ ,  $\text{Hg Cl}_2$ , and sodium.

3.—From Phenyl arsenious oxide and  $\text{Hg Cl}_2$ .

4.—From phenyl magnesium bromide and  $\text{Hg Cl}_2$ .

5.—From phenyl hydrazine and mercuric oxide.

6.—From phenyl mercuric iodide and sodium amalgam.

Also from phenyl mercuric bromide and  $\text{K}_2\text{S}$ , and from phenyl mercuric acetate and sodium stannite.

The compounds react in much the same way as the alkyl compounds do; thus it reacts with halogens, metals, and chlorides, non-metallic halides, acids, mercuric salts, organic halides, acid anhydrides, with sulphur and with oxidising agents.

Other phenyl mercuric compounds deserving mention are phenyl mercuric hydroxide, chloride, bromide, iodide formate

propionate, acetate, cyanide, nitrate, sulphate, carbonate and sulphocyanide.

Among the tolylmercuric compounds we have o mercury di tolyl, o tolyl mercuric chloride and nitrate, m mercury di tolyl, m tolyl mercuric nitrate, m mercury di tolyl, m tolyl mercuric chloride and bromide, p mercury di tolyl, p tolylmercuric chloride, bromide and iodide, and p tolylmercuric acetate and corresponding nitrate.

The benzyl mercury compounds worthy of note are: mercury di benzyl prepared from benzyl magnesium, chloride and mercuric chloride, and benzylmercuric chloride prepared from mercury di benzyl and alcoholic  $\text{Hg Cl}_2$ . The corresponding bromide, iodide, and acetate have been described.

Mercury derivatives of higher benzene homologues are known, for instance:

Mercuri bis 3, 4 dimethyl benzene,

„ 2, 4 „ „

„ 2, 5 „ „

„ 2, 4, 6 tri methyl benzene.

Mercuri bis penta methyl benzene, and mercuri bis 2 methyl 5 isopropylbenzene have been described.

Mercury derivatives of cyclo hexane are known; for instance, we are acquainted with cyclo hexylmercuric chloride, the corresponding bromide, cyanide, and sulphide. Among the mercury derivatives of aromatic nitro compounds, we have o nitro phenyl mercuric chloride prepared from nitro benzene and mercuric acetate; m and p nitro phenyl mercuric chloride. A compound of this class worthy of note is anhydride of o nitro benzal dimercuric hydroxide.

Mercury derivatives of sulphonic acids have been prepared, and mercury derivatives of phenylacetylene are described by various workers, but compounds which do deserve mention are the derivatives of naphthalene. A typical example of these is a mercury di naphthyl, which is obtained when a bromonaphthalene is heated with xylene and sodium amalgam in a pasty condition on an oil bath for some 20 hours. It reacts with acids, metals, halogens, mercuric salts, oxides of nitrogen, with arsenious chloride and thionyl chloride.

Other compounds of this class worthy of mention are:  $\alpha$  Naphthyl mercuric chloride bromide, iodide, formate, acetate, butyrate, nitrate and sulphide,  $\beta$  naphthylmercuric halides and sulphide.

We have now to consider one of the most interesting groups of organic mercury com-

pounds, namely, the mercury compounds of aromatic amines, which constitute one of the largest families of the mercury compounds.

The first compounds to be considered are the double compounds of aniline and mercury salts. Typical of this class are what are known as "mercuric chloride compounds." When aniline and  $\text{HgCl}_2$  in alcohol are mixed, we obtain a white crystalline compound,  $(\text{C}_6\text{H}_5\text{N H}_2)_2 (\text{Hg Cl}_2)_3$ ; other compounds of this kind are:  $(\text{C}_6\text{H}_5\text{NH}_2)_2 \text{Hg Cl}_2$ ,  $\text{C}_6\text{H}_5\text{N H}_2 \text{Hg Cl}_2$ , and  $\text{C}_6\text{H}_5\text{N H}_2 \text{H Cl Hg Cl}_2$ . Corresponding mercuric bromide, iodide, nitrate, cyanide and chlorate compounds are mentioned in the literature of the subject. In 1875, while studying the action of aniline on alcoholic solutions of mercuric chloride, Wislicenus prepared a yellow white, very insoluble compound,  $\text{C}_6\text{H}_5\text{N Cl Hg}$ . The compound was named "phenylated white precipitate," and was studied very thoroughly by Forster.

This brings us to the study of the true compounds of aromatic amines, p amino phenylmercuric acetate is a typical compound and can be prepared from N. mercuri aniline and acetic acid, aniline acetate, mercuric acetate, or from aniline acetate and mercuric oxide, or from aniline and mercuric acetate, the last being the usual method of preparation; it is essential to use freshly distilled aniline. The compound reacts with halides, can be acetylated, further, it can be diazotized and coupled, also it reacts with dinitro phenylhydrazine and with propargylacetate.

p Mercuri bis aniline is another aniline derivative of note, and can be prepared from p amino phenyl mercuric acetate and sodium thiosulphate, from p aminophenyl-arsenious oxide and sodium hydrate and mercuric chloride, also from p mercuric bis acetanilide, by heating with alcoholic potassium hydroxide.

p Amino phenyl mercuric hydroxide and its anhydride are obtained by dissolving p amino phenyl mercuric acetate in dilute  $\text{K O H}$  and treating with concentrated (30 per cent.) caustic potash.

p Amino phenyl mercuric chloride exists in both crystalline and amorphous forms, and reacts with sodium thiosulphate, dinitro diphenyl pyridine chloride, propargylacetate, and also with ethoxy acrolein acetal.

Other aniline derivatives are p amino, phenylmercuric bromide, iodide, nitrate

acid sulphate, sodium p aminophenyl mercuric thiosulphate, o aminophenyl mercuric acetate and chloride, 2 amino 5 nitrosophenyl mercuric chloride, 2, 4 diacetoxymercuri aniline.

Mercury compounds of nitroanilines are known; for instance, nitro aniline reacts to yield 4 acetoxy mercuri 2 nitro aniline, and 4, 6 diacetoxy mercuri 2 nitroaniline. Mercury derivatives of monomethylaniline and dimethylaniline are known. Examples are, p methyl aminophenylmercuric acetate, p mercuri bis monomethylaniline, p nitro o acetoxymercuri monomethylaniline of the first, and p mercuri bis dimethylaniline p dimethyl amino phenylmercuri acetate, hydroxide chloride, and of the second, p bromo dimethylaniline reacts to yield o acetoxy mercuri p bromo dimethylaniline is prepared from o nitro dimethylaniline.

In a similar manner, as examples of derivatives of ethylaniline, we have:

p Mercuri bis monoethylaniline, p ethylaminophenyl mercuric acetate, hydroxide and chloride.

For derivatives of diethylaniline we have p mercuri bis diethylaniline, p diethylaminophenyl mercuric acetate, hydroxide and chloride.

As examples of mercury derivatives of acid anilides we have:

N mercuri bis formanilide;

N mercuri bis acetanilide; and

p Acetaminophenyl mercuric acetate, p mercuri bis diphenylamine, p hydroxy mercuri diphenylamine, p mercuri bis methyl diphenylamine are derivatives of diphenylamine, 2 acetoxy mercuri phenylglycine ethyl ester.

$\text{Ac O Hg C}_6\text{H}_4 \text{ N H CH}_2 \text{ CO}_2 \text{ C}_2\text{H}_5$  is an example of an anilide fatty acid derivative.

2 Chloromercuri phenyl  $\alpha$  aminopropionic ethyl ester  $\text{Cl Hg C}_6\text{H}_4 \text{ N H CH (CH}_3\text{) CO}_2 \text{ C}_2\text{H}_5$  is another example.

Mercury derivatives of the three toluidines have been described; as examples of such we have:

3 Methyl 4 aminophenyl mercuric acetate;

Dihydroxy mercuri o toluidine;

Diacetoxy mercuri m toluidine;

Tri acetoxy mercuri m toluidine.

Acetoxy mercuri p toluidine;

Hydroxy mercuri p toluidine;

Chloro mercuri p toluidine.

Other amino aromatic derivatives of mercury are:

Acetoxy mercuri dimethyl p toluidine;

p Acetoxy mercuri o aceto toluidide,



Dichloro mercuri o aceto-toluidide;  
 p Acetoxy mercuri m acetotoluidide.  
 The anhydride of o hydroxy mercuri-p  
 acetotoluidide.

Di acetoxy mercuri o tolyglycine ethyl  
 ester;

o Acetoxy mercuri p tolyglycine ethyl  
 ester;

p Benzylamino phenyl mercuric acetate;  
 2, 4 Diacetoxy mercuri and naphthyl-  
 amine; and

2 Acetoxy mercuri naphthionic acid.

## ODOUR CONDITIONS.

By JOHN MISSENDEN.

To place into categories the various substances which produce odour, to enumerate definite values for these substances, and to define some tangible link between odiferous bodies and their chemical properties, a certain amount of postulation is essential. Referring to the works of Berthelot, Kremer, Durrans, Tyndall, Linné, and others, one finds such a wide divergence of views as to render these problems seemingly incapable of solution. Indeed, the assertions of some that no measureable linkages exist are almost justifiable. If, however, all these investigations and opinions are collated, and their substance combined with the results of later research, a working hypothesis and tabulation becomes practicable, and might form the base of more intensive and expert examinations within the next few years.

The first consideration is that of the physiological conditions governing the organs of smell, with the chemical conditions being interdependent. In the first place, all substances that can be detected by the olfactory senses must be volatile;<sup>1</sup> consequently, the *intensity* of odour may be practically determined by *degrees of volatility*. In the second place, the substances in their volatile state must be capable of solution in the lipinous fluid of the olfactory organs, and their *degree of solubility* therein determines the remaining component of intensity. And, in the third place, there must be some *chemical reaction* with the lipinous fluid; this would determine the *quality* of the odour.

Three conditions, then, based upon the most fundamental facts which are already common knowledge, provide working data. Their tabulation is as follows:—

- (a) degree of volatility: \_\_\_\_\_)
- (b) degree of solubility in lipins: \_\_\_\_\_) intensity;
- (c) chemical reaction with lipins: \_\_\_\_\_ quality.

### (a)—DEGREE OF VOLATILITY

While a substance, to be odiferous, must be volatile, it does not follow that all volatile substances are odiferous. Water, for instance, is volatile; yet it is said to be odourless. If this datum is regarded from a relative standpoint, water becomes odiferous, inasmuch that it dilutes the lipinous fluid, thereby causing quite a perceptible olfactory state when present in sufficient quantities.

Volatility may be measured by loss of weight over a standard period of time. If this period be taken as  $1 \times 10^{10}$  hours, and the amount of the substance be standardised as 1,000 grams, a range of numerical values would result under uniform conditions of temperature and pressure. Suppose trinitrobutyltoluene be selected as an example. According to Berthelot's calculations, 1 gram of this body will lose about

1  
 — grams of its weight in one hour in order  
 $10^{15}$

to be detected by the olfactory senses. That is to say, if the suggested standard be adopted, the degree of solubility would

1  
 be 0.01. Iodoform, losing about —  
 $10^{12}$

grams per hour, would lose about 10 grams of its weight (1,000 grams) in  $1 \times 10^{10}$  hours in simple rate, or  $10e$  grams at compound rate, where  $e$  is the exponential. This is the value when iodoform is just discernible, and would obviously vary according to the sensitiveness of the olfactory organs. The difficulty may be overcome by calculating the value at *maximum* volatility at N.T.P.

Peisse<sup>2</sup> has arranged all known perfumes in graded degrees of volatility, and a useful indication of relative losses of weight may be derived therefrom. Woker<sup>3</sup> made some observations upon the dependence of volatility upon intramolecular tension, and suggested that the intensity of odour was increased in direct ratio. This is so to a certain extent, but due allowance must be made for the solubility of a substance in the lipinous fluid, as it has been found that some highly volatile bodies are almost insoluble in lipin—hence practically odourless. Pyrocatechin,  $C_6H_4(OH)_2$ :(1:2), is a case in point.

## (b)—DEGREE OF SOLUBILITY IN LIPINS.

The theory, part of which has since become an incontrovertible fact, that an odiferous substance must be soluble in water and lipins, emanated from Backman.<sup>4</sup> His theory is correct in the case of water, otherwise how can he account for the odour of volatile oils? Whereas these oils are known to be soluble in lipins, they are totally insoluble in water. Both water and the lipinous fluid undoubtedly assist each other, but they are by no means indispensable to each other for all substances, if for some.

Investigation has not provided one instance of where a substance, either concentrated or dilute, which is insoluble in lipinous fluid, possesses odour; while there is much evidence to show that lipin-soluble substances always affect the olfactory nerves in a perceptible degree, providing a sufficient quantity be present. Such substances as bornyl acetate, phenol, and thiocyanide compounds stand in good contrast to mercury (odourless) and pyrocatechin (scarcely perceptible).

There are a number of properties, too numerous to discuss in detail within such a paper as this, which govern the activities of lipin. One finds, for instance, that chlorine, on conversion into a chloride, loses the greater part (if not all) of its odour; and solubility, combined with volatility, accounts for the decrease. The reasons for the change have been discussed by Teudt,<sup>5</sup> and by Ungerer and Stoddard,<sup>6</sup> who more or less claim that odour is dependent upon the rate of molecular vibration. Heller<sup>7</sup> energetically condemns the hypothesis; nevertheless, it is a sound one—but only as one of the conditions producing odour, and governing intensity.

## (c)—CHEMICAL REACTION WITH LIPINS.

Some very interesting postulatory work has been executed by Linné, and Zwaardemaker, who endeavoured to classify the qualities of odours. The term "odoriphor"<sup>8</sup> was introduced, which corresponded with the "osmophoric group" of Rupe and Majewski,<sup>9</sup> and the "aromatophors" of Klimont.<sup>10</sup> Many other terms have been introduced.

The quality of an odour (*i.e.*, whether it is aromatic, repulsive, and so forth) may be determined by the results of interaction with lipinous fluid, and not by the rate of interaction. At the same time, some overlap in these definitions is unavoidable: as in the instance of ammonia. Ammonia produces a pungent odour which is objec-

tionable; firstly because of the vibratory speed of interaction, and secondly because the residual products of interaction violently attack the subcutaneous tissue through the pores. The first, which imparts a sensation of burning, denotes intensity; the second is quality.

The determination of residual products after interaction with the lipinous fluid is of great importance, therefore, and all too little work has been carried out in this direction. Some observations have been made very much along the lines of Zwaardemaker's postulations, except that the nomenclature has been adjusted to correspond with that of Rupe, Majewski, Klimont, and others. The names have been placed in columns, as under, the first of which represents the new nomenclature, the second is that of Zwaardemaker, the third contains exemplary compounds, and the fourth the obsolete name.

I.	II.
Etherophors.	Ethereal odours.
Aromatophors.	Aromatic odours.
(a) Camphoraceous	
(b) Almond.	
(c) Citral.	
Enosmophors.	Fragrant odours.
Ambrosophors.	Ambrosaiacs.
Aldylophors.	Allyl odours.
Empyreumatophors.	Empyreumatics.
Hireinophors.	Hireon odours.
Kakosmophors.	Repulsive odours.
Fœtidophors.	Fœtid odours.
III.	IV.
Ether, etc.	
Eucalyptol.	Aromatophors.
Acetophenol.	
Cyclic limonene.	
Floral extracts.	Enosmophors.
Trinitrobutyltoluene.	"
Allyls and cacodyls.	"
Durene, etc.	Kakosmophors.
Fatty acids.	Odoriphors.
Quinoline, etc.	Kakosmophors.
Skatol, etc.	"

It will be appreciated that any attempt at sharp classification has not been attempted, although the various qualities are clearly separated on the whole. M. Appui, of St. Etienne (to whom I am much indebted for very valuable assistance, and who is now engaged upon the lipin reactions) has suggested that the fœtidophors be sub-divided into "pungent" and "irri-

tant," but I do not think that the two classes would be sufficiently defined, as the majority of pungent odours are also irritant.

(d)—GENERAL OBSERVATIONS.

Although it is impossible to trace any connection between odour and one chemical condition, the correlation of several conditions renders classification more practicable. The intensity of an odour can be measured, once standards are adopted, as the product of the values of volatility and solubility; while the classes under which the residual products fall after interaction with the lipinous fluid determines quality. In the evolution of some standard hypothesis, full credence can be given to Teudt's theory, although this is but a subsidiary factor. The known laws governing volatility, solubility, and chemical change will, regarded *en masse*, be the laws which govern odour, and it is hoped that this may prove to be the correct foundation for a more complete survey of the subject; in addition to which some satisfactory conclusions on the question of taste may be formed.

REFERENCES:

- <sup>1</sup> A gas is classed as a volatile substance.
- <sup>2</sup> *Des Odeurs des Parfums et des Cosmétiques*, 1865; *Perfumery Record*, 1919, p. 268.
- <sup>3</sup> *J. Physik. Chem.*, 1906, p. 456.
- <sup>4</sup> *J. Phys. Path. gen.*, 1917, p. 1.
- <sup>5</sup> *Chem. Gen.*, 1919, p. 138.
- <sup>6</sup> *Ung. Bull.*, 1922, III., 7.
- <sup>7</sup> *Amer. Per.*, 1920, p. 365.
- <sup>8</sup> *Arch. Neer. Phys.*, 1920, p. 224; *Abs. Chem. Soc.*, 1920, II., 75.
- <sup>9</sup> *Ber. Deut.*, 1900, p. 3,401.
- <sup>10</sup> *Die syn. und iso. Arom.*, 1899.

[BRITISH SCIENCE GUILD PUBLICITY SERVICE.—PAMPHLET No. 2.]

THERMIONIC VALVES.\*

By DR. J. A. FLEMING, F.R.S.

EARLY DISCOVERIES.

In the history and development of the

\* Readers of "The Chemical News" will no doubt be interested in one of the practical applications of electrons as apart from their functions in chemical processes. We have pleasure in here publishing "in toto" Pamphlet No. 2, issued by the British Science Guild, being "Thermionic Valves and Their Uses," by Prof. J. A. Fleming, F.R.S.

wonderful instrument called the Thermionic valve is to be found a striking example of the important industrial applications that sometimes follow from discoveries which take place in the course of purely scientific researches. In 1883 Edison sealed into the ordinary electric incandescent lamp in use for domestic lighting purposes a metal plate between the legs of its carbon filament. This plate was carried on a wire sealed through the wall of the glass bulb. He noticed that when the filament was made incandescent by a direct current sent through it, simultaneously a small electric current could be observed to be flowing through any delicate current-detecting instrument joined up in a circuit between the positive terminal of the filament and the wire carrying the metal plates; on the other hand, when the same instrument was in a circuit between the negative end of the filament and the plate, there was no sensible current. This phenomenon was called the "Edison Effect," but no explanation of it was given by its discoverer, nor was any practical use made of it at the time.

Scientific investigations on the nature of this "Edison Effect" were undertaken by me, beginning in 1883, and the discovery was soon made that this effect was connected with the projection in straight lines of particles from the filament. Sir William Preece, in 1885, communicated to the Royal Society a paper on this effect, and there was another paper by me in 1889, in which last it was shown that these projected particles carried a charge of negative electricity and could convey negative electricity from the filament to the plate, but not in the opposite direction. A long paper on this subject was sent by the present author in 1896 to the Physical Society of London.

A further step in advance was made about 1897 by Sir Joseph Thomson, the present master of Trinity College, Cambridge, who, whilst carrying out his remarkable researches in the Cavendish Laboratory, found that the chemical atoms of matter which at the time were thought to be incapable of being divided, were built up of still smaller atoms of electricity, now called electrons, and it was soon definitely ascertained that the incandescent filament of the ordinary electric lamp is continuously sending out a vast number of these little electrons in all directions.

All these achievements were purely scientific, and attracted no popular attention.

About 1897 the application by Senatore

Marconi of Hertzian Electric Waves for the purposes of wireless telegraphy began to create public interest. For detecting these waves he first used his improved form of the coherer of Branly and Sir Oliver Lodge. It was, however, rather capricious and somewhat difficult to manage, and Marconi soon replaced it by his magnetic detector in 1901.

#### INVENTION OF THE THERMIONIC VALVE.

In Marconi's system of wireless telegraphy, the electric waves are generated by creating powerful vibratory currents of electricity in a wire called an aerial wire stretched up through the air. The electric oscillations in this wire produce in surrounding space an effect called an Electric Wave, which travels outwards with the speed of light, viz., 186,000 miles per second. When these waves cut across another similar wire, called a receiving aerial, they create in it feeble electric vibrations of the same type.

In considering this matter, in researches carried out at University College, London, on Wireless Telegraphy, in 1904, I saw that if means could be found of converting the very rapid to and fro, or alternating, movements of electricity in the receiving circuits into a uniform motion of electricity in one direction, it would then be possible to detect them, and therefore the electric waves, by the use of the telephone or galvanometer as in ordinary telegraphy, without the use of a coherer. The vibrations of electricity in wireless telegraph aeriels are, however, very rapid, even up to a million per second, and none of the devices for "rectifying" or converting slow alternating electric currents into direct currents are of any use. Recalling to mind, however, my scientific investigations on the Edison Effect, I found on experiment that, if a metal cylinder was placed around the filament inside the vacuous bulb of an electric lamp carried on a wire sealed through the bulb, this appliance could "rectify" and therefore detect by the aid of a telephone or galvanometer the feeble high frequency oscillations of electricity. These cannot directly affect a telephone, because of their rapid reversals of directions thousands of times per second, but the instrument above described acts as a *valve* when placed in the path of these oscillations, and converts them into motions of electricity in one direction in virtue of the fact that negative electrons are passing in the vacuous space

only from the filament to the surrounding metal cylinder.

I therefore named this appliance an *oscillation valve* and subsequently a *thermionic valve*.

Later, in 1909, I suggested the use of tungsten as the material for the filament in place of carbon, as it withstands a higher temperature and emits more electrons.

The above described two-electrode or hot and cold electrode thermionic valve was soon extensively adopted as a means of rectifying and detecting electric oscillations and detecting wireless waves.

In the spark system of wireless telegraphy then exclusively used, the waves come in little groups of 20 or 30 with longer intervals of time between the groups. The Fleming valve rectifies the groups of oscillations produced in the receiving aerial into short gushes of electricity in one direction, and when these are passed through a telephone they gave rise to a more or less musical sound which can be cut up by a key in the transmitter into *dot* and *dash*, or short and long sounds making signals in the Morse Code.

#### SUBSEQUENT IMPROVEMENTS.

In 1907 an addition was made to the author's oscillation valve by Dr. Lee de Forest, who had been following in the United States very carefully the work done on this subject. Dr. de Forest introduced into a low vacuum valve a grid or zig-zag of wire between the filament and the plate. This started a new line of development, and it was found that, if a cylinder of metal gauze or spiral of wire was introduced into the hard or high vacuum Fleming Valve between the cylinder and the filament, it enabled the device to act as an amplifier of oscillations as well as a detector, so that very feeble high frequency oscillations could be magnified five or ten times by its aid. This suggestion was developed practically by the resources of the Western Electric and General Electric Companies of America.

This modified form then became known as a *three-electrode valve*, and is sometimes called for shortness a *triode*, or other trade names. To employ it as an amplifier we have to connect a high tension battery giving, say, 40 to 140 volts with its negative pole joined to the filament and its positive pole to the plate. A torrent of electrons is then forced from the filament, through the holes in the grid or gauze to the plate. If,

however, a feeble electrification is given to the grid positive or negative it increases or decreases this electron current. The grid potential electrification can be obtained from any two points on a circuit in which a feeble high frequency current flows, and the variation of the plate current of the valve will follow the variations of its grid potential. A number of such valves can be used in series and inter-connected by suitable induction coils or transformers and the plate current variations in one valve made to create changes of grid potential in the next valve. By a series of such coupled amplifying valves, we can then magnify in any required proportion feeble electric oscillations. It is the invention of this detector comprising a series of amplifying valves which has given us a detector of electric oscillations so enormously sensitive that wireless signals can be detected by it at the antipodes of the sending station and enabled us to signal half round the world by its aid.

(To be Continued.)

#### FLASHING POINTS.

By FRANK BROWNE, F.I.C.

Attention is drawn to the dangerous nature of highly inflammable liquids of low flashing point, of which class ether, benzol, carbon disulphide, benzoline and petrol are typical. Their flashing points (close test) are between  $-11^{\circ}$  and  $-30^{\circ}$ . Liquids with such low flashing points continuously give off inflammable vapour. The vapour from each is about 2.5 times heavier than air. Consequently, on a warm, still day, this vapour flows from an open tin of the liquid on to the floor, and may be drawn towards a flame situated at a distance of 30 feet by the air current produced by the heat. Then also the heavy vapour may pass through flooring into a danger zone in a room below, or it may flow downstairs. Users and the public, both on land and sea, should recognise these dangerous properties, and take measures accordingly. Where such a liquid is being used there should be no flame within a distance of 50 feet. A store should be ventilated both at top and bottom. Water being useless, a good supply of sand should be available for putting out a fire. Vessels containing these liquids might usefully be labelled. "In case of accident, smother fire with sand, earth or cloth."—(From the "Pharmaceutical Journal," 1923, p. 305.)

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

A meeting of the Society was held on Wednesday, October 3rd, at the Chemical Society's Rooms, Burlington House, W.

Papers read:—

*The Sampling of Coal; the General Problem and some Experiments*, by J. H. COSTE, F.I.C., E. R. ANDREWS, F.I.C., and W. E. F. POWNEY, F.I.C.

*A New Test for distinguishing Castor Oil*, by H. G. STOCKS, F.I.C.

*The Volumetric Estimation of Vanadium in Steel*, by A. E. ETHERIDGE, B.Sc., F.I.C., M.B.E.

*The Iodimetric Determination of Sugars*, by C. L. HINTON, F.I.C., and T. MACARA, F.I.C.

#### THE CHEMICAL SOCIETY.

ORDINARY SCIENTIFIC MEETING, THURSDAY, OCTOBER 4.

The following papers were read:—

*A Revision of the Dissociation Constants of Weak Inorganic Acids. Part I.: Boric Acid*, by E. B. R. PRIDEAUX and A. T. WARD.

*A Revision of the Dissociation Constants of Weak Inorganic Acids. Part II.: Phosphoric Acid*, by E. B. R. PRIDEAUX and A. T. WARD.

*Two Heterogeneous Gas Reactions*, by C. N. HINSHELWOOD and C. R. PRICHARD.

*A Homogeneous Gas Reaction. The Thermal Decomposition of Chlorine Monoxide. Part I.*, by C. N. HINSHELWOOD and C. R. PRICHARD.

*The Direct Union of Oxygen and Sulphur*, by R. G. W. NORRISH and E. K. RIDEAL.

*Note on Aqueous Formaldehyde Solution*, by W. R. ORMANDY and E. C. CRAVEN.

*The Interaction of Potassium Tetroxide with Ice and with Dilute Sulphuric Acid*, by H. HAWLEY and H. J. S. SAND.

## BRITISH DYESTUFFS.

An important letter on the above subject by Prof. W. M. Gardner appeared in the *Yorkshire Post* on September 12, from which the following is taken:—

“ At the recent general meeting in Manchester of the British Dyestuffs Corporation (Limited), the Chairman indicated that the policy of the directors for the present would be not to strive after new discoveries, but to develop the cheaper manufacture of known products. This decision has led to the resignation of the chief research chemist of the Corporation.

“ It must be recognised that the directors are faced with enormous difficulties. Their capital charges and production costs are excessively high owing largely to conditions beyond their control; bad trade has greatly reduced the demand for their products in this country, and what export trade there is is subject to the competition of Germany, Switzerland, and the United States. Dye users are strongly urging reduction in prices, and the shareholders in the Corporation have hitherto received a very meagre return. Under these conditions the directors are bound to adopt all possible economies which do not militate against ultimate success, and having spent £400,000 on research work during the past four years they propose to curtail such work in the future.

“ Two questions are involved. Is this policy the correct one; and, if not, what is the defect in the organisation which has led to its adoption?

“ With regard to the first point, the past history of the industry is very illuminating. It originated and was developed here for some years, but soon migrated to Germany, mainly because the large profits made were used here as dividends, but in Germany were utilised for research and works development. This fact, and the disastrous consequences of a repetition of the policy, have been pointed out again and again by those who have made a special study of the question.

“ The declared policy of the Corporation seems to be a repetition of the policy of the early sixties, which led to the shipwreck of the British dye industry in the early days. It is diametrically opposed to the policy which had led to success elsewhere. And, in expending £400,000 in four years on research, the Corporation has only been fulfilling an essential condition. In

the successful manufacture of dyes research is as essential as raw material and special machinery, and, appositely enough, the *Board of Trade Journal* of August 30 (p. 216) gives the official figure of 21 million dollars as having been expended on dye research in the United States during the past five years. It is well known, also, that one of the large German colour works, the Dadische Co., expended upwards of £900,000 on research on the synthetic production of indigo alone. Research is the lifeblood of colour manufacture, and the only wise policy in bad times is to intensify the work, which will lead to the introduction of new and valuable products from which a rich harvest will be reaped. To curtail research is to admit defeat by Continental and American competition. . . .”

## GENERAL NOTES.

## GERMANY'S POTASH INDUSTRY.

The Commercial Secretary at Berlin (Mr. H. N. Sturrock) has forwarded to the Department of Overseas Trade a report from the *Industrie und Handels Zeitung* of September 5, which states that the year 1922 was a record one for the potash industry, the sales of pure potash increasing from 460,591 tons in 1921 to 647,722 tons in 1922, or 40 per cent. From a report on industry, by the *Commerz und Privatbank*, it is clear that the enormous increase of potash sales in 1922 was in part due to a covering in advance, having regard to the currency depreciation and to anticipation by customers of a further nominal increase of potash prices. During the first months of 1923, customers showed a certain reserve—a natural reaction after large purchases, and partly due to the anticipated stabilisation of the mark. When it became clear that this could not be maintained, the demand of German agriculture set in on such a scale that in June the highest monthly sales so far recorded by the potash industry were effected, viz., 90,000 tons  $K_2O$ . In spite of these large sales, the level of the previous year has not yet been reached, but it is assumed that the difference will be made good during the following months, provided no unforeseen circumstances arise. Foreign countries, in particular, should contribute thereto, as foreign sales in 1923 have so far been satisfactory. The fact must not, however, be lost sight of that difficulties of sale in the potash indus-

try would arise immediately if the costs of production were rapidly adjusted to the gold parity, but foreign exchanges were to show a sinking tendency. In such case, the potash industry would doubtless feel the competition of the Alsatian works on the world's market seriously. As before, the American and Dutch markets are the most important customers for German potash.

The income of the industry, measured by distributed profits, is, of course, as in the case of the whole of German industry, extremely meagre, particularly in proportion to the gold capital invested in it.

The present policy of concentration has proved exceedingly successful, and has resulted in a considerable reduction of the costs of production. Only thus has it been possible to keep the inland prices of potash comparatively low, so that the increase as compared with pre-war times is considerably less than in the case of other comparable products of German industry.

#### PITCH FOR BRIQUETTES.

Mr. R. L. Nosworthy, H.M. Consul at Turin, reports that a local railway company is in the market for a considerable amount of pitch for use in the manufacture of briquettes (mattonelle carbone).

U.K. firms desirous of receiving further particulars regarding this matter should apply to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1, quoting reference 20579/F.W./M.C.2.

#### INTERVIEWS WITH THE COMMERCIAL SECRETARY AT BELGRADE.

Capt. E. Murray Harvey, O.B.E., Commercial Secretary at Belgrade, will be in attendance at the Department of Overseas Trade on October 1, 2 and 3, for the purpose of interviewing manufacturers and merchants interested in trade with the Serb-Croat-Slovene Kingdom.

Such interviews will only be given by appointment, and applications should be addressed to the Comptroller-General, Department of Overseas Trade, 35, Old Queen Street, London, S.W.1. In all cases the reference 4937/T.G. should be quoted.

#### BRITISH FLOUR MILLERS' RESEARCH ASSOCIATION.

The Secretary of the Department of Scientific and Industrial Research begs to announce that a licence, under Section 20 of the Companies' (Consolidation) Act, 1908,

has been issued by the Board of Trade to the Research Association of British Flour Millers, which has been approved by the Department as complying with the conditions laid down in the Government scheme for the encouragement of industrial research.

The Secretary of this Association is Mr. G. H. Ball, LL.B., 40, Trinity Square, E.C.

#### NOTICES OF BOOKS.

*Practical Chemistry for High Schools*, by H. B. DUNNCLIFF, M.A., B.Sc., A.I.C. Pp. IX. + 279. London: Mac-Millan & Co., Ltd., St. Martin Street, W.C.2. 1923. 5s.

There are now so many reliable textbooks on practical chemistry that a new publication should possess some outstanding feature to justify its appearance.

In the case of the present volume, which is presumably intended for young students who have not previously studied chemistry, it is difficult to find anything strikingly original in the matter or the presentation of the subject.

Indeed, certain passages might well have been improved upon from the teaching standpoint, and the book leaves the impression of having been hastily compiled.

Certain of the experiments are headed *Demonstrations*, and are apparently to be performed by a demonstrator at the end of the ordinary practical work. It will come as a surprise to most chemists to find that the first experiment for the beginner is the ignition of  $CS_2$ !

On page 25, in the section on the use of pipette and burette, quite complicated mathematics (involving the volume of a sphere) is introduced. The reviewer's experience is that even the simplest chemical calculations require careful presentation to young pupils.

Most of the illustrations are good, others, e.g., the distillation apparatus shown on page 17, could be clearer.

The old method of folding a filter paper is shown on page 32, but there is no mention of the modern practice.

On page 67 the author gives several definitions of an acid which he terms incorrect. They are really *incomplete*, and it would have been better to have explained this to the student. In the same chapter the Ionic Theory is dismissed in a few lines, and there is no further reference to ions in the rest of

the book, and not one ionic equation is given.

For some reason, the Qualitative Analysis Tables for identifying metals are duplicated, and this part of the book seems over-burdened with tests and re-actions.

These points, in the reviewer's opinion, detract from the value of a volume which is intended for use in schools. J.G.F.D.

*Field Crops in South Africa*, by H. D. LEPPAN, B.Sc.A., and G. J. BOSMAN, B.Sc.A. Pp. IX. + 358. Johannesburg: Central News Agency, Ltd., South Africa. 1923. 21s. net.

The time is rapidly approaching when the food production of the world will become a matter of urgent importance.

In his volume, *The Wheat Problem*, published in 1898, the late Sir William Crookes drew attention to the wasteful methods of cultivation and the risks this entailed. Other authorities have also emphasised the need for scientific methods in agricultural practice.

There is, fortunately, increasing evidence of the successful application of scientific methods to crop production, and this is not restricted to Great Britain. The present volume by Messrs. Leppan and Bosman indicates that considerable progress is being made in the Union of South Africa.

The subject of agronomy is treated in its various branches in as comprehensive a manner as possible. The authors have taken into consideration the chemistry, physics and biology of the soil in relation to plant culture. They also indicate the effect of changes in temperature, humidity, air currents, and light upon growth, and devote due attention to the questions of adaptation, breeding, and control of pests. Reference is made to the advances in these various branches of the subject which have been made by the Experimental Stations in South Africa.

The principal summer crops include maize, sorghums, potatoes, lucerne, various legumes, cotton, and sugar-cane. Winter crops include cereals and roots.

By reason of its extremely diversified climatic conditions and peculiar economic factors, agriculture in South Africa presents a great variety of problems. Doubtless considerable progress will continue to be made in the cultivation of those crops most suited to the country.

Those interested in the subject and wishing to consult this important volume can procure it from the English agents, Messrs.

Gordon & Gotch, 15, St. Bride Street, E.C.4.

*Alloys Resistant to Corrosion—A General Discussion*. 1923. The Faraday Society, 10, Essex Street, W.C.2. Price 5s. 6d.

*Recent Developments in Atomic Theory*, by LEO GRAETZ (Professor of Physics in the University of Munich. Pp. XI. + 174. 1923. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C.2. 9s. net.

## New Patents.

THIS list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Specifications Published this Week.*

203013—Thwaité, A. H., and Pease & Partners, Ltd.—Apparatus for drying, grinding, and neutralising sulphate of ammonia in one operation.

203015—Saltrick, W. R.—Extracting and refining metals and alloys.

203051—Soc. of Chemical Industry in Basle.—Manufacture of 2:3-diamino-anthraquinone.

203059—Murdoch, D. G., and Galbraith, W. L.—Reduction of organic compounds, particularly of nitro and azo-derivatives.

203124—Petroff, G.—Production of phenol aldehyde condensation products.

181014—Pollak, Dr. T.—Manufacture of condensation products from urea or its derivatives and formaldehyde.

202678—Cocksedge, H. E.—Process and manufacture of a sodium compound and a new composition containing the same.

*Abstract Published this Week.*

200760—Alkali thiosulphates.—Koppers Co., of 800, Union Arcade Building, Pittsburg, U.S.A.

*Abstract Published this Week.*

201302—Synthetic drugs.—Farbwerke vorm. Meister, Lucius, & Bruning, Hoechst-on-Main, Germany.

4-Amino-2-argentomercaptobenzene-1-carboxylic acid is obtained by reacting upon 4-amino-2-mercaptobenzene-1-carboxylic acid with a silver salt. The product, in the form of its alkali salts, is efficacious in the treatment of diseases caused by bacteria; it forms an N-methyl-w-sulphonic acid with formaldehyde and bisulphite, and can be diazotized and coupled with R-salt. In an example the reaction is effected with silver acetate in aqueous acetone containing ammonia; the solution is poured into a mixture of acetone and spirit and the product filtered, dissolved in diluted ammonia and the free silver compound precipitated by acid; ammoniacal silver chloride, silver fluoride, or silver nitrate may be used in place of the acetate.

4-amino-2-mercaptobenzene-1-carboxylic acid is obtained by diazotizing 4-nitro-2-amino-benzene-1-carboxylic acid, treating with potassium and cuprous sulphocyanides, and reducing the nitro-sulphocyanobenzene carboxylic acid.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3313.

## IS THERE AN ELEMENT OF ZERO ATOMIC NUMBER?

PART IV.

BY F. H. LORING.

In continuation of the above subject—*The Chemical News*, 1923, CXXVI., pp. 307, 325, 369—attention may be drawn to another line of study, but before proceeding with this development, it is considered necessary to refer to an abstract of the first two papers, which appeared in *Science Abstracts* for September, page 618, as follows:—"It is suggested that a single electron might be regarded as representing an atom with atomic number zero, since the atomic number represents the number of protons in the atom, and a single electron of course contains no protons." The italics are the present writer's. Continuing the quotation in order to refresh the mind of the reader as to the general scheme of arrangement involved in the argument—"If the existence of an active element with atomic number zero is assumed, and if the number of active elements below each of the inert gases is subtracted from its atomic number, the series 0, 1, 2, 3, 4, 5 is obtained, &c."

Now it was not the writer's intention to convey the idea that the atomic number was exactly represented by the number of protons in the atom, as obviously the existence of isotopes on first thought renders such an idea impossible; in fact it was explicitly stated that the electrons in the nucleus of the atom conditioned it in terms of atomic number—see bottom of page 325 *et seq.* (See also Aston's "Isotopes," pages 106, 107.)

It is evident, however, that the existence of sub-atoms of zero atomic number of mass 1 might bring about such a state of affairs, and no doubt the abstracter gathered this idea from the argument as presented. This view becomes an interesting possibility, but it will suffice merely to call particular attention to it here.

In *The Chemical News* of July 26, 1912, vol. CVI., p. 37, the present writer showed that the periodic table could be partitioned into a series of 5 natural groups, as follows: Inert gases; Group VIII.; Group Pr to Lu;

Grouping Cu, Ag, Au, to Br, I, —; The remaining elements.

The numbers of elements in these respective groups and groupings were given as 8, 9, 13, 20 or 21, 43, the sum being 92.83 by a formula given for calculating them. This was in 1912, before the atomic numbers were known. Had the atomic numbers been known at the time, the radio-elements would have been fully included in the scheme. The term *element* is now used in the atomic-number sense in discussions of this kind.

If now an element of zero atomic number is introduced at the head of the inert gases, it could, of course, be the electron as an element in one sense, for, like the inert gases, its atoms do not appear to combine with themselves, since they (the electrons) repel each other: but they are in other ways active.

Another view is, however, possible, and that is to consider an element of neutral property as if an electron had combined closely with a proton. This was discussed in Part III. (p. 369) of this series of papers. This will be referred to again below.

It will be seen from the foregoing that there should be 7 inert gases; 9 elements of Group VIII.; 13 elements of Group III. after cerium, generally referred to as the rare-earth series (extended series to be more precise); 21 elements, of which Cu, Ag, Au, are the left-hand members; and finally, 43 elements, the left-hand members of which are the alkali elements and including hydrogen and those of atomic numbers 72, 73, 74, 75, 87, 88, 89, 90, 91, 92.

Of course, some of the elements now represented by gaps may exist in very small relative quantities, as already discussed in these pages—see *The Chemical News*, 1922, vol. CXXV., pp. 309, 386; 1923, vol. CXXVI., p. 1.

Considering another cognate matter, coronium is known in the sun, but it is not known on the earth, so that it is in the nature of events to expect future discovery in this connection to throw some light upon the problems here discussed.

To show the trend of modern thought, the following, from page 157 of a new book just published, *Recent Developments in Atomic Theory*, by L. Graetz, translated from the German by G. Barr, is of interest in relation to these matters. In this exposition, Rutherford [see the writer's *Atomic Theories*, pp. 48, 49] remarks that it is possible that two hydrogen nuclei [protons]

with one electron might form the nucleus of another atom, which would then have a mass 2 and a nuclear charge 1, so that it would be an isotope of hydrogen. But there might also be a structure, consisting of a hydrogen nucleus and a negative electron, in which the electron was not, as in the hydrogen atom, at a great distance from the nucleus but directly adjacent to it. Such a structure would be electrically neutral except in its immediate neighbourhood. At the same time it would have a certain linear shape, and would orient itself in a definite direction in a magnetic or electric field. The possibility is not remote that what we call æther—which is, as is well known, a very bugbear in physics—might perhaps consist of such a doublet. The linear extension of this structure [lines of force?] would in particular afford an explanation of the fact that æther propagates electric and magnetic disturbances in the form of transverse vibrations. It would then also be conceivable, according to an idea of Nernst's, that under certain circumstances hydrogen atoms might be generated out of the æther, or, conversely, hydrogen atoms might be absorbed into the æther. Lodge (*Nature*, Aug. 4, 1923) has suggested that electrons are generated and absorbed in a similar way, involving the transformation of the energy of radiation. This is, of course, speculation, but there are many phenomena known to-day which make such ideas worth serious study.

The following points may be noted in connection with this study:—

1.—5 main groupings represented by the number of elements in each one.

2.—There may be 7 inert gases or members of the first group of this series, thus:

Rn, Tn, An (emanations)	At. No.	86	(1)
Xenon	" "	54	(2)
Krypton	" "	36	(3)
Argon	" "	18	(4)
Neon	" "	10	(5)
Helium	" "	2	(6)
Zero Element?	" "	0	(7)

3.—The other numbers, 9, 13, 21, 43, are, together with those above (7), in additive agreement with the atomic-number series; and they all stand in the right order as regards average chemical activity.

4.—The probable fact that there will be some gaps in the periodic table which will never be properly filled is in agreement with the "place principle" involved in the Bohr-Rutherford atom theory; and in conformity therewith the groups and groupings

as herein evaluated include such gaps. Nothing is in conflict, however, with the atomic-number-series classification of the elements in any of these studies.

5.—The three inert radio-active gases are isotopic, but each one being inactive chemically this isotopic character rests only on atomic number, so one is tempted to raise the figure to 8 or 9, according as the "zero element" is included or not, but the balance of the evidence seems to favour the lesser number, 7.

6.—The question whether the zero member can be an atom of æther, or the electron, or a close combination of a proton with an electron, or perhaps the element coronium, makes the subject an intensely interesting one.

[BRITISH SCIENCE GUILD PUBLICITY SERVICE.—PAMPHLET No. 2.]

THERMIONIC VALVES.\*

By DR. J. A. FLEMING, F.R.S.

(Continued from Page 221.)

THE THERMIONIC OSCILLATION GENERATOR.

The thermionic valve in its two and three-electrode forms possesses the power not only of rectifying and detecting electric oscillations, but also of creating so-called continuous or undamped oscillations. This discovery at once rendered possible radio-telephony on a large practical scale, whereas it had previously only been an occasional feat of experts. The proper coupling through a transformer of the grid and plate circuits results in the production in these circuits of self-sustained oscillations by energy drawn from the plate circuit.

During and since the war, improvements have continually been made in the construction of large generating valves. Beginning originally with very small powers of a few watts in valves with bulbs like incandescent lamps, very large valves in glass bulbs the size and shape of Rugby footballs, yielding an output of 6 or 7 kilowatts, are now made. Valves of 10—20 kilowatts ut-

\* Readers of "The Chemical News" will no doubt be interested in one of the practical applications of electrons as apart from their functions in chemical processes. We have pleasure in here publishing "in toto" Pamphlet No. 2, issued by the British Science Guild, being "Thermionic Valves and Their Uses," by Prof. J. A. Fleming, F.R.S.

put or more have been made with bulbs of silica. The most recent advance in this direction has come to us from the United States. A method of making high power valves with pulbs partly of glass and partly of copper has been developed by the Western Electric Company of America, based on the fact that a copper tube with a sharp edge can be welded to a glass tube. In large valves a source of trouble is the heating of the metal cylinder by the bombardment of the electrons. In the metal bulb valves the copper part forms also the anode cylinder, and it can be kept cool by immersion in water. Large generating valves of 10 to 100 kilowatts have been made in this manner, and the General Electric Company of America are said to be preparing a thermionic generating valve of the two electrode or Fleming type with an output of 1,000 kilowatts, or 1,300 horse power. If this can be done, large thermionic valves will replace high frequency alternators entirely in long distance wireless stations. Already Marconi's Wireless Telegraph Company have a Valve Panel of 56 large glass valves in their Carnarvon Radio Station with which communication is made direct to Australia. The present public Wireless Telephone broadcasting stations in Great Britain employ large valve generators in their transmission plant.

#### MODERN WIRELESS TELEPHONE AND TELEGRAPH VALVE RECEIVERS.

The improvements made in the construction of the thermionic valve and the close study of its action imposed by the necessity for developing wireless telegraphy and telephone during the great European War have given us an extraordinarily sensitive and easily managed detector of electric waves, and the advent of wireless telephone broadcasting has created a novel trade in the manufacture of these valves for generating, amplifying and detecting electric waves.

In the receiving valve most commonly used, a straight filament of tungsten, or thoriated tungsten, or else platinum-iridium, coated with oxides of barium and strontium, is used. This is surrounded by a spiral wire forming the grid and by a nickel or molybdenum cylinder forming the plate. The ends of the filament, grid, and plate are connected to pins on a cap so that the valve can fit into a socket like an electric lamp.

In modern wireless telegraph receivers, one or more valves are used to amplify the oscillations; one to detect, and one or more to amplify the rectified currents.

Valves of this type were made to the number of three or four million during the war (1914—1918), and are manufactured now by the hundred thousand per annum for wireless broadcasting purposes. Large factories employing hundreds of workers are devoted to their manufacture.

#### THE THERMIONIC TELEPHONE REPEATER.

An additional great service the thermionic valve renders is as a perfect telephone relay or repeater. Telephone electric speech currents are enfeebled by flowing along a telephone wire, and for long distance working very thick and therefore costly wires were required. Thermionic amplifiers can, however, be inserted in the run of line to re-enforce the currents so that they start on a further journey with fresh strength. By the use of these repeaters, telephonic speech is now transmitted right across the Continent of America (4,000 miles), and they are being now much used by the British Post Office. For shorter distances a great economy in copper can be obtained by their use. It would be feasible to speak from London to Delhi if it were worth while to erect the line and repeater stations. In short, the thermionic valve has effected a revolution in ordinary telephony just as it has made possible wireless telephony.

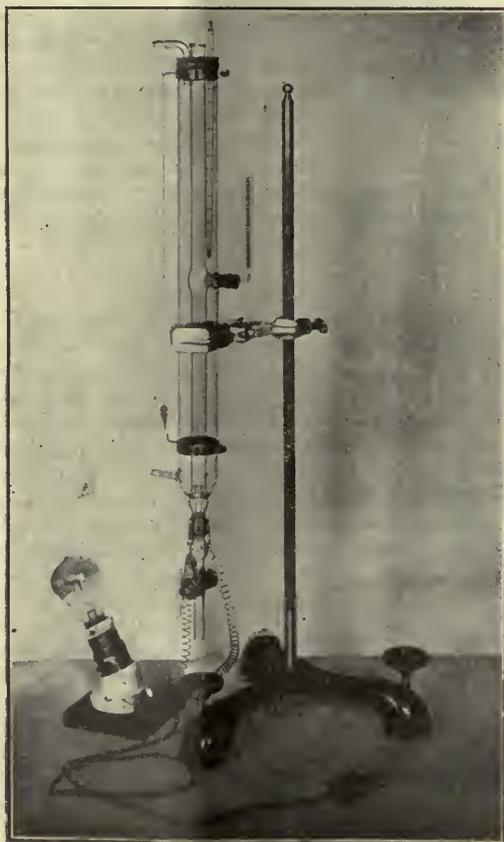
#### CONCLUSION.

It will be seen, therefore, that out of purely scientific researches and discoveries by Edison, Fleming, J. J. Thomson, Irving Langmuir, Lee de Forest, the invention of the two-electrode thermionic valve by the author in 1904 and the subsequent development of these discoveries by the expert investigators of great commercial organisations such as the Western Electric, The General Electric, The Marconi Wireless Telegraph, The Osram Lamp and Edison Swan Electric Lamp Companies, an immense industry has been built up, which, starting from very small beginnings when the first Fleming valves were made at the Edison and Swan Electric Lamp Works in 1904, and the Steam Electric Lamp Works, England, in 1907, has attained now (1923) enormous proportions and created an industry which has yet a great future before it.

## A RELIABLE APPARATUS FOR THE RAPID ANALYSIS AND REGULATION OF HIGHLY VISCOUS SUBSTANCES.

By DR. GUSTAV F. DIERFELD.

Hitherto there has been a considerable lack of apparatus for quickly analysing and regulating the application of highly viscous substances like varnishes for graphic purposes, lacquers, tar products, varnishes composed of pitches and oils, glue gelatines, collotions, etc. Analyses of this kind were generally performed by feeling or touch, whereby many mistakes took place, and a required correction could not be effected in a quick and reliable manner resting on calculation, and very troublesome difficulties and loss of time and money could be incurred in the course of further working. Dr. Robert Fischer, jointly with the Franz Hegershoff-works in Leipzig (Germany), has now designed a very cheap, easily heated apparatus, making possible a thoroughly reliable and exact analysis of



highly viscous transparent and opaque substances within the shortest time and under variable conditions.

This apparatus consists of an external glass tube, a cooling apparatus containing a thermometer, has a plumb-line on one side, and is supported by a stand (see the figure).

Within the outer glass tube a narrower one is arranged, open at its upper end and provided at its lower end with a cock and at its right side with a short glass tube shaped like an elbow, that contains another thermometer and leads through the surrounding external glass tube. A contact device arranged in the inner tube a little above the cock may be connected with an incandescent lamp or electric bell, jointed with an electric lead. For testing a viscous substance, the apparatus is at first adjusted by means of the plumb-line and the adjusting screws of the stand, so that it has an exactly vertical position. Then the external tube is filled up with water at 70° S. (158° Fahr.) that is cooled down to 62° C. (143.6° Fahr.). The temperature of this heating liquid is observed by means of the thermometer, arranged in the external tube or cooling apparatus, which makes a uniform heating of the apparatus possible by means of a constant supply of warm water. Meanwhile, about 100 grams of the substance to be tested (*e.g.*, glycerine) are warmed up to 70° C., and a sufficient quantity of this liquid is poured into the inner tube from above up to the destined stroke, and is cooled down to 58° C., as indicated by the aid of the thermometer in the elbow-like short glass tube. As stated, the difference of temperature of 4° C., and the temperature of the liquid to be tested of 58° C., is always the same. A small ball of aluminium or brass is then let fall through the upper open end of the inner tube; this tube is enlarged at the spot of its wall, opposite to the elbow-like glass tube, so that this ball is not turned from its proper way. By means of a stop-watch the time of falling of the ball in the liquid up to the lying on the contact device is determined. This time amounts to 4 seconds with glycerine of a known quality used generally as gauging liquid for gaining a decided footing. This value, 4, is the unit for the temperatures 62°-58° C.

Another substance, showing at the same difference of temperature with a time of falling of 16 seconds for the same ball, has a viscosity of 4, compared with the above, *i.e.*, its viscosity is four times greater.

falling ball touches the contact device, the lamp lights up or the bell rings, and at this moment the stop-watch should be read. In very thin or diluted liquids the time of falling of the normal ball may be so little that mistakes of observation may occur, and may cause a considerable error. To avoid this and to increase the time of falling by a multiple, Dr. Fischer utilised small balls of different size, three of aluminum and three of brass—according to the less or greater viscosity of the substances to be tested. Of course, in such cases, the apparatus is to be specially gauged for each of the balls.

Whilst a bright, transparent liquid is tested in such a manner whereby the falling of the ball is distinctly visible for examining dark-coloured, opaque substances, the apparatus is connected with the incandescent lamp or electric bell; as soon as the

From this work it is possible to compile tables, containing the numbers for different mixtures, for the adjusting of lacquers, varnishes, etc. A single number is then sufficient for showing full particulars of the viscosity of each substance. This procedure is more reliable than the usual one for samples of different substances, which frequently transform or deteriorate in the course of time. As admitted by experts, this apparatus of Fischer's has been used with success for the most varied industries.

## ORGANIC MERCURY COMPOUNDS.

### PART III.

By R. F. HUNTER, F.C.S.

(Continued from Page 217.)

We have now to consider the derivatives of phenols and related compounds, derivatives of aromatic ketones and terpenes, derivatives of aromatic acids, and lastly, the derivatives of heterocyclic compounds.

The first to be considered are the phenol, naphthol derivatives, etc.

o Chloromercuri phenol.—The first typical compound is usually prepared along with the m and p compounds by the action of mercuric acetate on phenol. It reacts with nitrous acid to yield p nitroso chloromercuri phenol. Other phenol derivatives are:

- p Acetoxy mercuri phenol;
- p Chloromercuri phenol;
- p Hydroxy mercuri phenol;
- Di acetoxy mercuri phenol;

- p Benzeneazo o acetoxy mercuri phenol
- and p dichloromercuri phenol;
- Mercuri bis o phenol;
- Mercuri bis o phenylacetate;
- Mercuri bis p phenylacetate.

Phenol ethers readily react with mercuric acetate, for instance, anisole has derivatives, such as:

- o Mercury Dianisyl;
- o Acetoxy mercuri anisole;
- p Mercury dianisyl.

With mercuric acetate anisole yields such compounds as p acetoxymercuri anisole.

o Mercury diphenetyl, o acetoxy mercuri phenetole, p mercury diphenetyl are derivatives of phenetole.

Phenetole heated with mercuric acetate yields p acetoxy mercuri phenetole.

As examples of mercury derivatives of substituted phenols we have:

- p Hydroxymercuri o chlorophenol;
- o Hydroxymercuri p chlorophenol;
- 4 Hydroxy mercuri 2 nitro phenol;
- 4 4' Mercuri bis 2 nitro phenol;
- 2 Hydroxy mercuri 4 nitrophenol;
- 2 Acetoxy mercuri 4 nitrophenol;
- 2 Chloromercuri 4 nitro phenol;
- Hydroxy mercuri picric acid;
- Chloromercuri picric acid.
- p Chloromercuri o aminophenol;
- 6 6' Mercuri bis 1 hydroxy 2 methyl benzene;

zene;

- 4 arsenic acid;
- o Acetoxy mercuri p cresol;
- o Iodomercuri p cresol;
- Diacetoxy mercuri p cresol;
- o Chloromercuri p cresol methyl ether.

As derivatives of the naphthols we have 4 acetoxy mercuri  $\alpha$  naphthol prepared from the action of naphthol in mercuric acetate in acetic acid solution;

- 2, 4 Diacetoxy mercuri  $\alpha$  naphthol;
- 1 Acetoxy mercuri  $\beta$  naphthol;
- 2 Acetoxy mercuri 1 naphthol 4 sulphonic acid and its sodium salt.

Derivatives of resorcinol have been prepared, for instance:

- Chloro mercuri resorcinol;
- Dichloro mercuri resorcinol;
- 6 Acetoxy mercuri 2 nitro resorcin.

The first mercury derivatives of the aromatic acids to be considered are those of benzoic acid and the anhydride of o hydroxy mercuri. Benzoic acid is typical, and is prepared by fusing mercuric acetate and benzoic acid until the reaction is complete.

- Derivatives of benzoic ester are:
- o Chloro mercuri benzoic methyl ester;

and *o* Chloromercuri benzoyl chloride.

As derivatives of substituted benzoic acid we have:

N - iso di acetoxy mercuri anthranilic methyl ester;

Ac O Hg C<sub>6</sub>H<sub>3</sub> (CO<sub>2</sub> Me) N H Hg O Ac  
H<sub>2</sub> O;

Acetoxy mercuri anthranilic methyl ester;

Iodo mercuri anthranilic acid;

5, 5' Mercuri bis 2 amino benzoic methyl ester;

6, 6' Mercuri bis 2 amino benzoic acid;

Chloromercuri methylanthranilic methyl ester;

Iodomercuri methyl anthranilic acid;

Acetoxy mercuri *p* amino benzoic ethyl ester.

The derivatives of cinnamic and salicylic acid deserve mention. Examples of the former are:

$\alpha$  Acetoxy mercuri  $\beta$  methoxy hydrocinnamic methyl ester;

$\alpha$  Mercuri di  $\beta$  phenyl anhydrohydracrylic acid;

$\alpha$  Acetoxy mercuri  $\beta$  ethoxy hydrocinnamic methyl ester;

$\alpha$  Acetoxy mercuri  $\beta$  isopropoxy hydrocinnamic methyl ester;

and of the latter case:

3 Halide mercuri 2 hydroxy benzoic acid;

Chloromercuri salicylic methyl ester;

Acetoxy mercuri salicylic methyl ester;

Mercuri bis salicylic ethyl ester;

3 Acetoxy mercuri 5 nitro salicylic acid;

5 Amino salicylic acid

are examples.

The derivatives of ketones and terpenes are not of great importance. We might mention:

Phenacyl mercuri chloride;

Phenyl *o* chloromercuri phenyl ethyl carbinol;

2 Hydroxy mercuri indandione as ketone derivatives.

2 Chloro mercuri cineol is an example of a terpineol derivative. As camphor derivatives we have:

$\alpha$   $\alpha$  Di iodomercuri camphor;

$\alpha$  Acetoxy mercuri camphor; and

$\alpha$  Halide mercuri camphor.

We have now to consider our last group of compounds, viz., the mercury derivatives of heterocyclic compounds.

Thiophene in acid solution reacts with the sulphate of mercury, giving a series of compounds.

Chloromercuri thiophene is obtained from thiophene in alcohol, saturated mercuric chloride and concentrated sodium

acetate solution. It reacts with halogens, acid halides, inorganic iodides, etc.

Other thiophene derivatives are:

$\alpha$  Iodo and bromo mercuri thiophene;

$\alpha$  Mercuri di thienyl.

As derivatives of substituted thiophenes we might mention:

5 Chloro mercuri 2 methyl thiophene;

5, 5' Mercuri bis 2 chloro thiophene;

5, 5' Mercuri bis 2 iodothiophene;

3 Chloromercuri 2, 5 dimethyl thiophene;

2, 5 Dichloromercuri 3 methyl thiophene;

2, 2' Mercuri bis 3, 4 dimethyl thiophene.

Among the compounds of this group which have been prepared, we have derivatives of indole, pyrazolones, for instance:

3 Methyl, 3, 4 diacetoxy mercuri 4 methoxy 1 acetoxy mercuri phenol 3, 4 dihydro 5 pyrazolone is a pyrazolone derivative. Cyclomercuri polymethylenes are said to have been prepared.

The mercury compounds have been reviewed. Anything like a full review is impossible in an article such as this. The field is a very big one, to say the least of it. No attempt has been made to describe the preparations. These can be found in Whitmore's excellent work and in the original papers. As with arsenic, compounds of lesser importance have sometimes been mentioned where more deserving ones have been omitted. This is inevitable in an article of this kind, but nevertheless, if the article has brought the subject to the notice of many chemists who have not previously had to deal with the subject, I shall feel satisfied. Again, as I said before, the article is a review, not a thesis, and a review, like charity, can be made to "hide a multitude of sins," and this being so I do not feel called upon to apologise for its incompleteness, and in many places, lack of experimental detail.

#### PRELIMINARY REPORT OF THE MINERAL PRODUCTION OF CANADA DURING THE SIX MONTHS ENDING JUNE 30, 1923.

The present report is issued in continuance of the policy of the Dominion Bureau of Statistics of preparing preliminary estimates regarding the production of the principal mineral products from Canadian deposits. Data are given showing the quantity and value of each metal produced and of each non-metallic mineral shipped.

Comparative figures are given for the corresponding period of the previous year and revised statistics for the calendar year 1922 have been included.

Measured in terms of the metallic and non-metallic mineral output and excluding structural materials and clay products, the mineral production of Canada during the six months ending June, 1923, was valued at \$87,152,248, as compared with \$60,361,109, the value of the corresponding production in the first six months of 1922. The output of these commodities during the twelve months of the calendar year 1922 was valued at \$144,762,501, so the records for the present year show that an appreciable advance has been made both in relation to the output in the first six months of 1922 and also to the entire calendar year.

The outstanding feature of the metal industry was the recovery in the production of nickel and copper. The re-opening of the smelters and refineries operated by the International Nickel Company and the British America Nickel Corporation resulted in a production of nickel during the first six months of the year which was nearly seven times greater than the production in the first half of last year, and the output of copper was more than double the quantity produced in the corresponding period last year. The copper output during the half-year was greater than the total production during the calendar year 1922; the nickel output was also nearly 60 per cent. greater than the entire quantity made during the twelve months ending December, 1922.

The production of gold and silver was maintained at about the same levels as in the corresponding period in 1922, while the outputs of asbestos, coal, lead and zinc were higher than in the first half of 1922. Shipments of gypsum, while less in amount were greater in value, and while the output of salt declined the quantity sold was greater than in the half-year ending June, 1922.

Power shortage was again experienced in Northern Ontario during the spring months, and it was not until the latter part of April and the beginning of May that enough power was obtained to permit capacity operation of the Porcupine mines. The three leading producers were reported early

in May as being in a position to treat approximately 7,000 tons of ore, the Hollinger treating about 5,000, the Dome 1,200, and the McIntyre 1,000. The operation of the enlarged McIntyre plant was also made possible by the additional power obtained about the beginning of May.

Power developments in Northern Ontario have been watched with considerable interest by the mining industry. Sturgeon Falls power is now available; Metachewan is expected to be operating by fall, and the developments on the Quinze River and by the Hollinger on the Abitibi River are being carried forward with a view to the elimination of the recurring spring power shortage that has handicapped these properties up to the present time.

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#### GENERAL NOTES.

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#### METAL FOR SYNTHETIC AMMONIA TUBES.

The tubes which contain the catalyst for synthesis of ammonia must support the action of compressed gases at temperature of 500 to 700° C. They have been made with alloys poor in carbon and containing nickel, chromium, tungsten or similar metals. The percentage of nickel may be 60 per cent. and more. According to a French invention by the Société Chimique de la Grande Paroisse a very soft iron, poor in carbon, can be utilised for hyper-pressure treatment. The composition of the iron is similar to that of dynamo and transformer plates. A metal employed for the purpose contained: Si, 0.018 per cent.; S, 0.09 per cent.; C, 0.098 per cent.; Mn, 0.93 per cent.

Thin round plates of this metal were subjected for hundreds of hours to the action of a mixture of N, H and NH<sub>3</sub>, at a pressure of 1,000 atmospheres and temperatures varying from 700° to 800° C., without displaying any sign of fragility. Such a metal can be employed for catalyser tubes, provided that suitable measures are taken to provide for the considerable decrease in tensile strength and the appearance of viscosity at temperatures above 500° C.—(*L'Industrie Chimique*, August, 1923.)

PROCEEDINGS AND NOTICES OF  
SOCIETIES.

THE CHEMICAL SOCIETY.

The following papers were read at the Ordinary Scientific Meeting, Oct. 4:

*Note on Aqueous Formaldehyde Solution*, by W. R. ORMANDY and E. C. CRAVEN.

Discrepancies in the published values for the densities of aqueous formaldehyde solutions probably arise from the presence of methyl alcohol. The densities of solutions prepared by refluxing with water are now found to agree excellently with the results of Auerbach and Barschall, who prepared solutions by volatilising paraform in a current of nitrogen and absorbing the gaseous formaldehyde in water. The density and the refractive index of a formaldehyde solution appear to be linear functions of the formaldehyde concentrations.

The specific refractivity of the formaldehyde in the dilute aqueous solution appears to be 0.205, which agrees well with the assumption that methylene glycol is formed, and this is also borne out by density measurements.

*The interaction of potassium tetroxide with Ice, and with dilute Sulphuric Acid*, by H. HAWLEY and H. J. S. SAND.

It was shown that only hydrogen dioxide results from the interaction of potassium tetroxide with ice or with dilute sulphuric acid.

*The Direct Union of Oxygen and Sulphur*, by R. G. W. NORRISH and E. K. RIDEAL.

The reaction of oxygen and sulphur has been studied by a dynamic flow method, between 235° and 385°. Below 305° it proceeds with a temperature coefficient of 1.63; above 305° this falls off rapidly, due to the secondary formation of sulphur trioxide. The reaction is limited to the surface of the sulphur and the walls of the vessel, and proceeds equally well on both, pointing to a liquid film covering the whole surface of the vessel.

A table of seven different reactions of sulphur was given, which shows that their critical increments are simple multiples of a constant quantity, which is considered to be the half value of the work required to create one free sulphur bond.

PROF. J. F. THORPE also read two papers dealing with the work of himself and his collaborators in the field of Isomerism and Tautomerism.

THE INSTITUTE OF METALS.

PROGRAMME FOR 1923-24.

The Institute of Metals has just issued its programme of meetings and lectures for the session 1923-24. There are over thirty lectures and addresses to be given before the Institute's local sections in Birmingham, Glasgow, London, Newcastle-on-Tyne, Sheffield, and Swansea, as well as at meetings of the parent Institute, one of the latter, including a lecture by Dr. F. W. Aston, F.R.S., which is to form part of the proceedings of next year's Empire Congress of Mining and Metallurgy.

The subjects of the lectures are of a character to interest engineers and metal workers, and include "Extrusion Problems," "Nickel Brasses," "Some Impressions of American Non-Ferrous Metallurgy," "Metals for Lamp Manufacture," "X-Rays and Metallurgy," "General Scientific Brass Foundry Work," "Alloys for use with Super-heated Steam," "The Density of Alloys," "The Annealing of Non-Ferrous Metals," "The Action of Molten Brass on Nickel Steel," "Propeller Brass," "Large Metallic Crystals and Some of their Properties," "The Cold Working of Metals," "Electric Resistance Furnaces," "Substitutes for Platinum," "The Metallurgical Microscope," and "Influence of Casting Temperature on the Physical Properties of Metals."

A ballot for the election of members of the Institute (whose membership covers that of the local sections), is due to take place shortly, and full particulars can be obtained from the Secretary of the Institute, Mr. G. Shaw Scott, M.Sc., 36, Victoria Street, London, S.W.1.

THE INSTITUTION OF PETROLEUM  
TECHNOLOGISTS.

*Recent Researches Bearing upon the Origin of Petroleum*, by E. H. CUNNINGHAM-CRAIG, B.A., F.R.S.E., F.G.S. (MEMBER).

Read at the Royal Society of Arts, on Tuesday, October 9.

The author dealt with some of the researches which have been undertaken, having a distinct bearing upon the origin of petroleum.

The genesis of petroleum has been variously attributed to:—A. Inorganic Origin: (1) Hypogene causes; (2) Vulcanicity. B. Organic Origin: (1) From animal matter; (2) From vegetable matter.



Of the inorganic origin there is little to be said.

This leaves the organic theories as rivals, that of animal origin being chiefly supported by chemists, while the vegetable origin theory is largely held by geologists, and has gained much ground in recent years.

There is a tendency to investigate the relations of coals and lignites to petroleum. Every country that contains either coal or petroleum, or both, can furnish some evidence, and it is becoming obvious that the two fuels have definite relations to each other.

The three main oil-bearing horizons in Trinidad have each a carbonaceous phase in some other district, and the two phases, petroliferous and carbonaceous, approach each other very closely in some localities.

Similar evidence has been forthcoming from many countries, *e.g.*, Venezuela, Burma, Assam, Hungary, and Roumania.

Much pertinent evidence from Great Britain was also brought to light by the work of the Petroleum Research Department during the war, but unpublished, and the relations of oil to coal and to oil-shale have been made clearer. Perhaps the most striking evidence is that afforded by the boring at D'Arcy, near Kalkcith. This well was drilled on the theory that oil-shale denotes petroleum that is dead and buried, but that beneath an oil-shale series some free petroleum may still exist.

By treating any coal containing a fair percentage of volatile matter with hydrogen under very high pressure and at temperatures up to 850° F., a remarkable exothermic action is induced and a portion of the solid fuel becomes liquefied, giving as a result a product indistinguishable from heavy crude petroleum. Similar effects can be obtained by hydrogenating heavy crude oils, lighter oils being formed. The work of Dr. Bergius, though perhaps hardly yet successful as a commercial proposition when coal is treated, or, as it is stated, "liquefied," has certainly opened up a vista of great possibilities. It appears that the percentages of volatile matter in the coal is one of the determining factors controlling the reaction, another being the pressure. Pressures as high as 3,000 and even 5,000 lbs. per square inch have been used, but action may commence with a pressure of no more than 600 lbs. Temperatures need not apparently be very high, but as the action is exothermic there is difficulty

in keeping it from rising too high. The reaction takes place in an autoclave.

The value and importance of these researches lie in their similarity to the conditions of the formation of oil. It has long been recognised that coal is a finished product, and that oils cannot be formed from it except by distillation.

The fact that the reaction is exothermic must not be lost sight of. External heating of the autoclave will retard the action, and the heat engendered by the action may be sufficient to check it and bring about an equilibrium. But in Nature, working slowly through countless periods of time, the rapid heating up of the material by an exothermic reaction will be obviated by conduction.

Prof. Flynn recently separated gels from the matrix by crushing a Nova Scotia torbanite and floating the gels in brine, so that they can be examined and analysed apart. The gels are tough rather than hard, and so resist crushing successfully; they are of large size and rough exterior, and are fresh and free from signs of inspissation. They contain from 16 to 20 per cent. of inorganic matter in a fine colloidal state. The inorganic content is quite conclusive proof that these gels are not vegetable fossils. This confirms the views advanced by the writer, and if oil shale denotes petroleum petroleum "still-born."

#### THE OPTICAL SOCIETY.

An Ordinary Meeting of the Society was held at the Imperial College of Science and Technology, Imperial Institute Road, on Thursday, October 11. The following papers were read and discussed:—

*Notes on the Elementary Algebraic Theory of a Class of Photographic Objectives*, by E. T. HANSON, B.A.

*A General Survey of the Thin Double Lens*, by T. SMITH, M.A., F.INST.P.

*New Types of Levelling Instruments using Reversible Bubbles*, by T. F. CONNOLLY, M.Sc.

#### JOURNAL OF SCIENTIFIC INSTRUMENTS.

The first regular monthly number of the *Journal of Scientific Instruments* produced by the Institute of Physics with the cooperation of the National Physical Laboratory, will appear on October 15.

SOCIETY OF PUBLIC ANALYSTS AND  
OTHER ANALYTICAL CHEMISTS.

ORDINARY MEETING.

Held at the Chemical Society's Rooms,  
on October 3.

Mr. P. A. Ellis Richards, President, in  
the chair.

Certificates were read for the first time in  
favour of:—

Messrs. Laurence Eversley Campbell,  
M.Sc. (Lond.), F.I.C.; John Troubridge  
Hannon, B.A. (Cantab), A.R.C.Sc., A.I.C.;  
Cyril Langley Hinton, F.I.C.; Douglas  
William Kent-Jones, B.Sc. (Lond.), F.I.C.;  
Thomas William Alan Shaw, M.Sc. (Liv.);  
William Hall Simmons, A.I.C.; Kenneth  
Edward Nethercoate Williams; Percy Noel  
Williams, M.Sc. (Liv.), A.I.C.

The following was elected a member: Mr.  
Robert C. Grimwood, A.C.G.F.C., D.I.C.,  
A.I.C.

The following papers were read:—

*The Sampling of Coal: the General Problem and some Experiments*, by J. H. COSTE, F.I.C., E. R. ANDREWS, F.I.C., and W. E. F. POWNEY, F.I.C.

Attention was drawn to difficulties encountered in sampling coal which is often a heterogeneous mixture, and in consequence of which the variations in composition of different "patches" are extremely wide. These variations are likely to be more extreme in those cases where the bulk is large and where it is impossible to sample throughout the dump.

General considerations that should govern the sampling were suggested, and stress was laid upon the point that if, as often happens, different workers obtain different results from samples taken from the same bulk, the discrepancies are not due to mistakes in working, but were indicative of the variability in composition of the coal. Experiments were described in which (1) it was shown how difficult it is to obtain a homogeneous set of samples from so small a quantity of coal as 70-80 lbs., and (2) the variation in composition of samples taken progressively from a bulk of about 400 lbs.

*New Test for Distinguishing Castor Oil from other Oils and determining its Purity*, by H. B. STOCKS, F.I.C.

Ordinary soap solutions are alkaline to

phenol-phthalein. On titration with standard acid solution a point is reached at which a state of equilibrium exists and the pink colour disappears. The amount of acid required increases with the dilution up to about 1 part in 150 or higher, at which point it becomes practically constant. With soaps of oleic, palmitic, and stearic acids, and soaps from oils composed of these acids, the figures are equivalent to approximately half the total combined alkali. With castor oil soap it is only 3 to 11 per cent. of the total. 5 grams of the oil to be examined are saponified with alcoholic potassium hydroxide, neutralised, evaporated to remove alcohol, made up to 100 ccs., 10 ccs. being diluted with 250 ccs. of neutral distilled water and titrated with hydrochloric acid in presence of phenol-phthalein. Castor oil gave figures varying between 4.8 and 7.9, and figures are given in the paper for a number of fats and oils and rosin, in each case very much higher than for castor oil.

*The Volumetric Estimation of Vanadium in Steel*, by A. T. ETHERIDGE, B.Sc., F.I.C., M.B.E.

The estimation is carried out in the same solution in which the chromium has already been estimated by treating the aqueous solution of the sulphates of the metals with permanganate, filtering, removing any colour due to iron, treating with standard ferrous sulphate solution and titrating with permanganate. This gives the chromium figure. The solution is then adjusted so that it contains about 10 per cent. by volume of sulphuric acid, excess of ferrous sulphate is added, and the solution titrated with potassium bichromate, using as indicator 5 cc. of diphenyl carbazide prepared by dissolving 0.5 grams in 1-2 cc. glacial acetic acid, and diluting to 500 cc., and adding to each 5 cc., 3 drops of 25 per cent. sulphuric acid, and 1 drop of potassium bichromate solution, resulting in the formation of a deep purple colouration. About half the indicator solution is then added and the end point occurs within 1 or 2 drops, with the formation of an apple green tint. It is necessary to have (1) a small amount of ferrous solution present at the time the indicator is added, (2) 10 per cent. sulphuric acid, (3) absence of nitric acid (except in traces).

*The Iodimetric Determination of Sugars*, by C. L. HINTON, F.I.C., and T. MACARA, F.I.C.

The aldoses, e.g., dextrose and lactose,

are quantitatively converted to the corresponding monobasic acids by iodine in alkaline solution at ordinary temperature, provided the proportions of alkali and iodine to sugar are suitably controlled. The slight oxidation of sucrose and levulose found by other observers is confirmed, and the extent of this action is shown to depend considerably on time and temperature of reaction as well as on the proportions of iodine and alkali used. Using standard conditions it is possible to determine sucrose accurately in mixtures by titration before and after inversion, but the determination of other sugars is liable to be affected by non-sugar reducing substances. The method is so convenient, however, that it recommends itself technically for approximate determinations of invert sugars.

#### CANADIAN ASBESTOS PRODUCTION.

According to the preliminary report on the mineral production of Canada, compiled by the Dominion Bureau of Statistics, the total asbestos mined during the first six months of 1923 amounted to 1,482,102 tons, of which 1,297,243 tons, or 87.5 per cent., was milled. Sales advanced to a total of 99,042 tons, valued at 3,574,762 dols., as compared with sales of 54,846 tons, valued at 1,894,232 dols. in the corresponding period of 1922.—*Board of Trade Journal*, October 4.

#### BRITISH INDUSTRIES FAIR.

In connection with notices recently published in certain daily papers, the Department of Overseas Trade states that the voluntary liquidation of the British Industries Fair (Birmingham) Incorporated, in no way affects the London British Industries Fair, organised by that Department. Nor will the liquidation of this Association and the transfer of the responsibility for the management of the British Industries Fair (Birmingham) to the Birmingham Chamber of Commerce prevent the holding of the 1924 British Industries Fair at London and Birmingham as usual. The London section will be open at the White City from April 28 to May 9, and the Birmingham section follows on May 12 to 28.

#### INTERVIEWS WITH H.M. SENIOR TRADE COMMISSIONER IN INDIA.

Mr. T. M. Ainscough, O.B.E., Senior Trade Commissioner in India, is at present in this country on an official visit, and will be in attendance at the Department of Overseas Trade during October for the purpose of interviewing manufacturers and merchants interested in trade with India. Such interviews will only be given by appointment, and all applications, quoting the reference 4814 T.G., should be addressed to the Comptroller-General, Department of Overseas Trade, 35, Old Queen Street, Westminster, S.W.1.

#### CAST IRON RESEARCH.

The Monthly Circular of the British Cast Iron Research Association contains valuable data on malleable iron, together with micros obtained from the research work in hand. This preliminary information should show the malleable industry how very essential it is to push forward a wide scheme of research. This early information will be supplemented in subsequent bulletins. Members only are privileged to obtain this information. Researches to discover a cast iron to resist corrosion are being carried out. Interesting data has been sent in by members, from which it is evident that the purposes for which cast iron was required to resist corrosion are fairly large.

#### THE EVOLUTION OF CHEMICAL TERMINOLOGY.\*

BY JAMES F. COUCH.

*Comme ce sont les mots qui conservent les idées & qui les transmettent, il en résulte qu'il seroit impossible de perfectionner la science, si on n'en perfectionnoit le langage.*—LAVOISIER.

The lack of ambiguity in the practical use of the term hydroxide may well occasion surprise that a consideration of this term has been included in this series of papers upon chemical terminology. There are few chemical terms more often used and certainly there is none which is used by

\* [Reprinted from "The American Journal of Pharmacy, Philadelphia, Pa., July, 1293.]

the chemist with more specific meaning. It is one of the first items of information that he receives in his elementary course in chemistry. It stares at him from his little shelf of reagents in the laboratory, and it would not be exaggeration to say that the first example of applied chemistry he learns is the broad principle that hydroxides neutralise acids and may, therefore, remedy accidents to fabrics. His most indispensable reagents are sulphuric acid and sodium hydroxide, and he comes to know these substances as a painter knows brushes and a sculptor knows marbles. The chemist grows up in science with the concept hydroxide; it is always with him; it is ever in use; it finally becomes immanent in his very nature. Why, then, should he not be completely familiar with it? Where is there possibility of ambiguity or misconception in the use of this term?

From the foregoing it is easy to believe that I have never met the chemist who does not cherish a conviction that he knows what a hydroxide is. It requires more courage, however, to supplement that assertion with the statement that I have not yet met a chemist who really does know what a hydroxide is, and, furthermore, it is not at all difficult to convince any reasonable chemist that his knowledge in this respect is incomplete. If he doubts this a very few adroit questions will serve to bring him to an impasse and demonstrate the fact.

Some months ago I set out to investigate this term hydroxide. The examination of available facts led to the astonishing conclusion that there is no general agreement in the definition of the term, so that, strictly speaking, unless one specifically modifies the word when he uses it, he says next to nothing definitely when he employs the term hydroxide. In other words, we have here a most flagrant example of indefiniteness. Here is a concept which is in daily use, which enters into a large portion of all chemical thought, which underlies and conditions many important chemical theories; and it lacks the *sine qua non* of scientific terms, precise meaning!

This fact immediately becomes apparent upon consultation of the dictionaries and the textbooks of chemistry. We find a diversity of opinion among authorities when, as is not always the case, they venture to define the term. Many writers of inorganic chemistries present no definition of hydroxide, but content themselves with

referring to the formation of basic hydroxide, but content themselves with referring to the formation of basic hydroxides through the interaction of water and alkaline oxides or by the reaction between sodium hydroxide and certain metallic salts. The various expressed views of the term hydroxide may be classified under four chief concepts: there is the view that these substances are compounds of water with oxides; fundamentally opposing this is the view that hydroxides are hydroxyl compounds and of this conception there are three main divisions: first, the idea that any hydroxyl compound is an hydroxide, second, the common notion which may briefly be stated thus, hydroxides are hydroxyl compounds of basic radicals, and third, a compromise between these extremes which allows the class hydroxide to embrace all hydroxyl compounds but prefers its application to basic substances.

The first view has few proponents to-day. It was, however, held by most of the early chemists and has been supported by very capable men. D'Aubuisson<sup>1</sup> in 1810 wrote:

"Mineralogists and chemists have too little fixed their attention on water considered as a constituent of minerals with the exception of those salts in which this substance has been remarked under the name water of crystallisation. Meanwhile the rocks of which it forms an essential constituent part are in great number; without mentioning those which compose the numerous family of the zeoliths I will cite the wavelite recognised by Davy and Klaproth as a true hydrate of alumina, composed of water and alumina in constant proportion. Diaspore . . . seems to be nothing but a hydrate of the same earth. The opal is probably only a hydrate of silica."

This quotation is interesting through the knowledge it gives us concerning conditions in chemistry a century ago. It appears that only a very few chemists had any real conception of the importance of water as a constituent in compounds and consequently it was too often overlooked. Berzelius,<sup>2</sup> however, grasped the significance of combined water, and in 1812 developed an hypothesis to explain it which influenced chemical thought for several decades. This was his notion of acid and basic water:

"Hydrate, oder Verbindungen des Wassers: Erstens: mit Säuren. In diesen spielt das Wasser ganz die Rolle einer Basis; die Säure nimmt davon zur Sätti-

gung eine Menge auf, welche genau so viel Sauerstoff als eine Salz-basis enthält, von der diese Menge Säure gesättigt wird.

"Zweitens: mit Salzbasen. Das Wasser spielt hier in so fern die Rolle eine Säure, als es ihre Stelle vertritt, enthält aber nur gleiche Theile Sauerstoff mit der Basis, oder ist zuweilen ein submultiplum vom Sauerstoff der Basis."

He uses the term hydrate freely, speaking of "Hydrate der Thonerde" and "Eisen Hydrate." Vauquelin<sup>48</sup> in 1813, repeating an analysis published by Prof. Bruce of New York, confirmed the findings of the American:

"It appears from this analysis that the mineral which formed the subject of it is simply a combination of magnesia and water (hydrate of magnesia)."

Vogel,<sup>49</sup> writing in 1818 "Sur les Hydrates," defined them thus:

"When water unites with a solid body and preserves with it the solid state, it is in this case, only, that one gives to the combination the name of hydrate."

He refers to soda and potash as hydrates, and mentions the hydrate of lead. None of these authors used the term hydroxide, for, at this time, it had not been generally accepted. Graham,<sup>23</sup> considering water as a constituent of salts, does not employ the term hydroxide, but he had the concept, for he distinguishes carefully between the water combined in acids and that in bases following the hypothesis of Berzelius already quoted. Thus Graham:

"In the hydrates of the caustic alkalis and of the earths, water is retained by a strong affinity, and is generally supposed to be united, like an acid, to the alkali or earth. In such hydrates water discharges an acid function."

"In the case of hydrates of the acids,\* the portion of water which is found to be inseparable by heat, or to be very strongly retained, has generally been presumed to be in the place of a base to the acid, although little attention has been paid to the subject. The most highly concentrated sulphuric acid retains one atom of water, and is supposed to be a sulphate of water."

\* It is hardly necessary to remind the reader that at this era the oxy-acids were not regarded as hydrogen compounds, but what we now term the acid anhydrides, or acidic oxides, were termed acids and the combinations of these oxides with water were called hydrates of the acids.

In the "Hand-Book of Chemistry" of Leopold Gmelin,<sup>20</sup> published in 1849, we begin to get a more definite statement about water-compounds; he defines oxides:

"The act of combination of oxygen with other bodies is called oxygenation (combustion); also acidification, when the resulting compound is of an acid nature; oxidation in the contrary case. The oxygen is the oxygenizing body (supporter of combustion); also, according to circumstances, the acidifying or the oxidizing body." v. 2, p. 38.

"Oxygen forms about 136 inorganic compounds; they are as follows:—

1. Of acid nature . . . . .
  - a. Non-metallic oxygen acids . . . . .
  - b. Metallic oxygen acids . . . . .
2. Compounds not of acid nature: Oxides." v. 2, p. 38.

Gmelin does not use the term hydroxide, which, indeed, was not common in Germany, the word hydrate being there used. It is clear, however, that his idea of hydrates was that of the modern concept of basic hydroxides, and there can be no doubt that, had the question been raised, he would not have extended the term hydroxide to include the oxy-acids. Silliman<sup>46</sup> is not so definite:

" . . . it combines with many substances, forming a large class of hydrates: hydrate of lime and potash are examples. It is also, as we have seen, essential to the acid properties of common sulphuric, phosphoric, and nitric acids, acting here the part of a much more energetic base than in the hydrates." p. 249.

He seems, nevertheless, inclined to limit hydrates to basic compounds. Newth<sup>27</sup> unequivocally assumes this position:

"Binary compounds that are formed by the union of elements with oxygen are called the oxides of these elements. Certain of these oxides are capable of entering into combination with water, giving rise to substances known as acids; such acids are distinguished as acid-forming oxides, or acidic oxides. They are also sometimes termed anhydrides. All the non-metallic elements, except hydrogen, form oxides of this order, and the acids derived from them are known as the oxy acids.

"Certain other oxides also unite with water, but give rise to compounds known as hydroxides. When such oxides, which are all derived from the metallic ele-

ments, are brought into contact with acids, chemical union takes place, and a compound termed a salt is formed. Such oxides are distinguished as salt-forming or basic oxides. There are also oxides which are neither acidic nor basic." p. 17.

These quotations serve to present a clear picture of the notion that hydroxides are water compounds and they show in addition the diversity of opinion in respect to the limits of application of the term. It will be observed that, while the term hydrate is used throughout in most of the citations, the writers clearly had in mind those compounds which to-day would be termed hydroxides. We turn then to the consideration of the view that hydroxides are hydroxyl compounds, and first examine the broadest application of this view.

This conception is not of very great age. It appears only a short time before the publication of the theory of ionisation. Fownes,<sup>50</sup> in 1885, and this is the earliest reference to this specific concept that I have found, says:

"Water acts on many oxides, both acid and basic, with great energy and considerable evolution of heat, producing compounds called hydroxides." p. 159.

Under "hydrates," the 1889 edition of Watt's "Dictionary of Chemistry," we read the following:

"Another way of stating the theoretical difference between hydrates and hydroxides is to say that hydrates contain water as such, and that hydroxides contain the elements of water." p. 703, v. 2.

"The term hydroxide is sometimes used in a narrower sense than explained above; by some chemists it is applied only to compounds whose reactions are best explained by supposing them to contain the group or radicle OH." p. 704. Remsen<sup>42</sup> in 1899 supported this view:

"... the hydroxides form two of the most important classes of compounds, known as acids and bases." p. 61.

Goodchild and Tweney<sup>21</sup> define an hydroxide thus:

"A compound containing the hydroxyl group OH. Hydroxides may be acid or alkaline in character." p. 298.

"Funk and Wagnall's Dictionary"<sup>17</sup> presents this definition:

"A compound containing the group hydroxyl, and formed by the union of the molecules of water, so that a rearrangement of the atoms takes place, yielding hydroxyl." p. 880.

The "Handwörterbuch der Naturwissenschaften," Jena, 1914, is in accord with this view.

"Hydroxyde kennt man Verbindungen welche die einwertige 'Hydroxyl' gruppe —OH enthalten. . . ." v. 5, p. 344.

The definition given by "Webster's"<sup>152</sup> is:

"A compound of an element or radical with hydrogen and oxygen, not regarded as containing water. . . . The term is usually applied, and by many chemists restricted, to compounds containing the group OH, or hydroxyl. Hydroxides may be basic, neutral, or acid, according to

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<sup>48</sup> Vauquelin, L. N.: *Annal. de Chim.*, 7, 32 (1817).

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<sup>23</sup> Graham, T.: *Phil. Mag. and J. of Sci.*, 3d. Ser., 6, 327-334, 417-424 (1835). *Trans. Roy. Soc. Edin.*, 13, Part I.

<sup>20</sup> Gmelin, L.: "Hand-Book of Chemistry," *Trans. H. Watts. London.*

<sup>37</sup> Newth, G. S.: "A Textbook of Inorganic Chemistry, 1898.

<sup>50</sup> Watts, H.: "Fownes Manual of Chemistry," 1885.

<sup>42</sup> Remsen, I.: "Inorganic Chemistry," Ed. 5, 1899.

<sup>21</sup> Goodchild and Tweney: "A Technological and Scientific Dictionary," 1906.

<sup>17</sup> "New Standard Dictionary of the English Language," 1909, 880.

(To be Continued.)

#### NOTICES OF BOOKS.

*The Chemistry Tangle Unravelling*, by F. W. GRAY, M.A., D.Sc. Pp. VIII. + 148. London: Longmans, Green & Co., 39, Paternoster Row, E.C.4. 1923. Price 6s. net.

Before opening this little volume, the reviewer called to mind the vast mass of experimental work that had given rise to multitudes of inorganic, as well as organic, compounds. On the other hand, there are the countless theories dealing with comprehensive, limited, or even trivial sets of experimental facts and fancies.

Dr. Gray's book is evidently an earnest endeavour of an ardent teacher to place before the student and drive home the essential fundamentals upon which the facts of Inorganic Chemistry are based.

At the present time there is urgent need for such a text-book, and in the main the author's attempt at unravelling the tangle has been successful. In doing so he has not hesitated to make use of the latest experimental results and theoretical deductions. He commences with the brief essentials of the historical development of the periodic classification of the elements, and including the subject matter and the latest information. Until recently, the periodicity of the elements was usually and most suitably represented by Mendeléef's Table. There are now other schemes (*e.g.*, Loring's Wedge Table, *The Chemical News*, 1922, CXXV., 387), and the author has incorporated a pyramidal scheme which he states is based on Langmuir's conceptions of atomic structure.

There are several minor points in which the reviewer feels that the volume might be improved to increase its general utility to students. It sometimes seems rather an account of the tangle than its unravelling. Thus, whilst avoiding a catalogue of facts, the author has gone to the extreme of assuming that the student already has a good general knowledge of them in his possession, even though they be in a tangle.

In the chapter entitled *Multiplex Anions and Multiplex Cations*, reference could be made to a number of bodies of very minor significance, and there is a tendency to coin expressions. Most of the information in the chapter on the Formation of Complex Ions is valuable and important, but the author is wrong in stating (p. 92) that magnesium chloride is the only chloride of group II. A which forms double chlorides. In the same chapter, the presence of water in certain double salts is disregarded.

Except at the end, there are no diagrams, which is a disadvantage, since these are very helpful in visualising various matters.

The author has undoubtedly produced a book which should stimulate a true interest in science in the students' mind, and those who take students through the labyrinths of advanced Inorganic Chemistry would probably profit by a perusal of this work.

J.G.F.D.

*Alloys Resistant to Corrosion*, a General Discussion held jointly by the Faraday Society and the Sheffield Section of the Institute of Metals, April 1923. Price 5s. 6d.

From time to time the Faraday Society arranges meetings for discussions on Physico-Chemical subjects of importance and interest. At these meetings papers are read and discussed by the eminent scientists who are invited and attracted.

Thus, in April last, there was a general discussion on *Alloys Resistant to Corrosion*, held jointly by the Faraday Society with the Sheffield section of the Institute of Metals, and the Manchester Metallurgical Society (an account of which appeared in *The Chemical News*, April 20, pp. 246-9). The contributions were subsequently published in the Society's Transactions, but in order to reach a wider public, are now reprinted in book form.

No definite theory of corrosion emanated from the discussion, but much valuable information was gathered together concerning the methods of prevention, etc.

The reprint is not only of interest to academic physicists and chemists, but also to engineers and technicians.

*Chemistry, Inorganic and Organic*, by CHARLES LOUDON BLOXAM. Eleventh edition, revised by ARTHUR G. BLOXAM, F.I.C., and S. JUDN LEWIS, D.Sc., F.I.C. Pp. IX. + 832. London: J. & A. Churchill, 7, Great Marlborough Street. 1923. Price 36s.

In Bloxam's chemistry, both the Inorganic and the Organic Sections of the science are considered in adequate detail and in one volume. This arrangement certainly has obvious advantages, especially from the point of view of the student who needs a general knowledge of the whole science. It is evident that the present authors had this in mind, since there is a long section on the general principles of Physical Chemistry which has been inserted following the treatment of the non-metals and preceding the chemistry of the metals.

The early chapters deal with water and its elements; the Air and its constituents and the general properties of Gases; hydrogen, occlusion, reduction, oxidation; the halogens; the sulphur, phosphorus, carbon and boron, and argon groups.

The treatment of the metals as based upon the Periodic Classification.

The chapters on organic chemistry follow the usual plan of arrangement, except that

aliphatic and aromatic substances are described together in the same chapter.

By incorporating both branches of the subject in one volume, the authors have been able to describe such organic metallic derivatives as the cyanides, simple and complex, in a chapter in the organic portion of the book. They have, however, given an account of acetylene, ethylene and methane in the inorganic section.

The section on physical chemistry gives a good account of the present position in that subject and, as might be expected, the chapter on spectroscopy is particularly good.

Whilst such a comprehensive volume as this lends itself to criticism on the grounds that some sections must receive better treatment than others, it must be admitted that this edition fully maintains the traditions of the previous ones.

#### BOOKS RECEIVED.

*From Determinant to Tensor*, by W. F. SHEPPARD, Sc.D., L.L.M. Pp. VIII. + 127. 1923. The Clarendon Press, Amen Corner, Paternoster Row, E.C.4. 8s. 6d. net.

*Radio-Activity*, by K. FAJANS, Professor of Physical Chemistry in the University of Munich. Pp. XII. + 138. 1923. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C.2. 8s. 6d. net.

*Kolloide in der Technik*, von DR. RAPHAEL ED. LIESEGANG. Pp. 157. 1923. Herr Theodor Steinkopff, Residenzstrasse 12b, Dresden & Leipzig.

We have received a copy of the *Year Book of the Michigan College of Mines, 1922-23*, which also contains announcements of the courses of instruction for the session 1923-24.

We have received a copy of the Prospectus of University courses in the Municipal College of Technology. It gives particulars concerning the College and its courses and examinations.

#### PAMPHLETS ISSUED BY THE UNION OF SOUTH AFRICA, DEPARTMENT OF AGRICULTURE.

*Notes on the Chemical Control of Cattle-Dipping Tanks*, by C. O. WILLIAMS, B.Sc. Pp. 137 + 141.

*The Estimation of Fineness in Basic Slag*, by DR. CHAS. F. JURITZ. Pp. 5.

*Some Analytical Methods*, by H. F. L. BISCHOFF and B. DE C. MARCHAND, B.A., D.Sc. Pp. 8.

*Some Observations on the Sulphate-Molybdate Method of Determining Phosphoric Oxide*, by V. A. BECKLEY and A. MARAIS. Pp. 5.

*Investigation of Different Methods of Testing Babcock Milk Bottles*, by C. O. WILLIAMS, B.Sc., A.R.C.S. Pp. 132 + 136.

*Representative Transvaal Soils. The High Veld Sandy Soil*, by B. DE C. MARCHAND, B.A., D.Sc. Pp. 6.

*The Composition of Some Indigenous Grasses*, by ALEXANDER J. TAYLOR, B.A. Pp. 218 + 232.



THIS list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

23557—Casale, L.—Production of catalysts for synthesis of ammonia. Sept. 20.

23570—Casale, L.—Apparatus for catalytic production of synthetic ammonia. Sept. 20.

23424—Dreyfus, H.—Manufacture of aliphatic compounds. Sept. 10.

23565—Fraymouth, W. A.—Recovery of calcium oxalate, &c., from trees. Sept. 20.

23231—Badische Anilin & Soda-Fabrik.—Manufacture of active carbon. Sept. 17.

23348—Badische Anilin & Soda-Fabrik.—Production of vat colouring-matters. Sept. 18.

203533—Badische Anilin and Soda-Fabrik.—Manufacture and production of dyestuffs and intermediate products therefor.

203551—Hovey, R. B., and Hovel, F. L.—Nitrate of lime.

#### Specifications Published this Week.

203352—Weizmann, C., and Blumenfeld, J.—Production of titanic acid.

203383—Perkins, W. G., and Beasley, W. H.—Production of refined copper from copper oxide.

186329—Parodi, P. Distilling apparatus for continuous operation.

#### Abstract Published this Week.

201786—Dyes.—Kalle & Co., Akt Ges., 23, Rhein-strasse, Biebrich-on-Rhine, Germany.

*Perylene derivatives*.—By treating perylene-3:4:9:10-tetracarboxylic acid, or a substitution product thereof, with ammonia or primary aromatic or aliphatic amines, it is converted into difficultly soluble imides which dye animal and vegetable fibre in fast red to blue-violet shades from the vat. In examples the acid or its ammonium salt is heated with ammonium carbonate, methylamine hydrochloride, or aniline; other suitable amines are *p*-chloraniline,  $\alpha$ - or  $\beta$ -naphthylamine,  $\alpha$ - or  $\beta$ -amino-anthraquinone, also diamines such as *o*-, *m*-, and *p*-phenylene-diamines, 1:8-naphthylenediamine, and benzidine. The perylene 3:4:9:10-tetracarboxylic acid may be prepared by oxidizing with hypochlorite, chromic acid or other oxidizing agent, the vat dyes made by alkali fusion of perinaphthindanone or perinaphthindandione.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract **only**, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3314.

## AN EXPLANATION OF THE THEORY OF THE ROTATION OF THE ATOMIC NUCLEUS.

### PART IV.

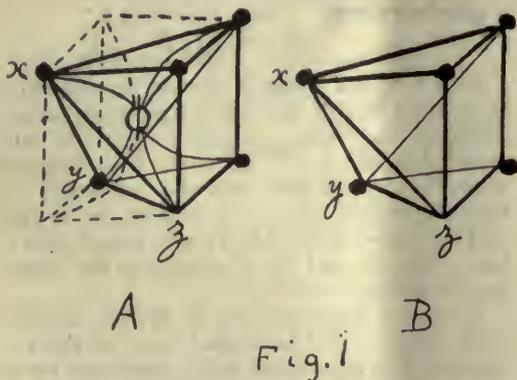
BY HERBERT HENSTOCK.

#### OXIDES (continued).

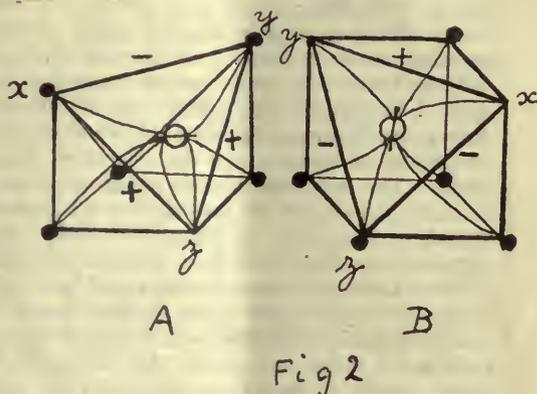
#### Group V.

Before discussing the oxides of this group and especially those of nitrogen, it will be necessary to examine the very interesting case of the nitrogen molecule itself. Presumably the two nitrogen atoms are linked by a treble bond, and in that case both atoms will have distorted octets, which would most probably take the forms described below.

If we take the positive nitrogen atom and distort it, as shown in Fig. 1 A, the dotted lines indicating the parts of the cube which will vanish, we should then have a figure as shown in Fig. 1 B.



If the whole of Fig. 1 B. be now turned through an angle of  $90^\circ$  so that the side  $xy$  of the triangle  $xyz$  comes uppermost, it will be seen as in Fig. 2 A. In order to form a treble bond the negative atom would be as shown in Fig. 2 B., and if this were taken up, turned over, and applied to the positive atom so that  $xy$  and  $z$  in each atom coincided, then the bond would be complete and the molecule of nitrogen would be formed.



On viewing this arrangement, several interesting points will be noticed.

- (1) The two atoms exhibit no free valencies.
- (2) Both cubes are distorted to the utmost, which the number of electrons will permit, in a similar way to carbon as represented by the tetrahedron.
- (3) No cube face is opened up in either atom in order to form the bond, such as occurs in the case of carbon-monoxide. Therefore the nitrogen molecule will be very stable, since a partial opening up encourages further opening up, so that the nitrogen molecule should be more stable than that of CO, which is, of course, the case.
- (4) The positive atom, if viewed as in Fig. 1 B., is seen to be identical in shape with that which the carbon atom has in carbon-monoxide. (See Part III., *The Chemical News*, 1923, CXXVII., 18.)
- (5) There are the same number of electrons in the combined octets of the nitrogen molecule as in those of CO.

In a paper by Bone, Hewitt and Townsend, read before the Royal Society (April 27, 1923), Professor Bone stated that, "In the combustion of mixtures of  $2\text{CO} + \text{O}_2$  with nitrogen as a diluent, the nitrogen exerts a peculiar energy absorbing influence, far beyond that of other di atomic diluents, and also that this energy absorbed is slowly liberated again as the system cools down." This absorption of energy may be due to the opening up of the octet of the positive nitrogen atom, which might go as far as the rupture of the treble bond with formation of a single bond or even the complete separation of the atoms, which would permit of the opening up of the full octets of both atoms, and thus leave them with three free and active valencies apiece, permitting their

union with other atoms such as oxygen. The same thing probably occurs when a high tension electric current is passed through air; in this case, considerable energy is required to produce this effect, and it is therefore more than probable that both these absorptions of energy are due to the same cause. The converse of this opening up process would occur on cooling, with consequent re-emission of energy. This also agrees with their further statement that "The nitrogen becomes activated and will combine with oxygen when in this state"; the activated condition is that in which the octets are reformed ready for union with other atoms, in fact the converse of the process shown in Fig. 1.

Again, they state that "If nitrogen is used as a diluent in exploding mixtures of hydrogen and oxygen, no such activation occurs, and that a small percentage of hydrogen introduced into a carbon monoxide-air mixture is sufficient to prevent it." They deduce from this that "The peculiar influence of nitrogen in  $2\text{CO} + \text{O}_2$  explosions is due to its ability to absorb the particular quality of radiation emitted when CO and oxygen (but not when CO, oxygen and hydrogen) react; such radiation is known to be of a different wave length from that emitted during the flame combustion of hydrogen. In other words, there seems to be some constitutional correspondence between CO and  $\text{N}_2$  molecules whereby the vibrational energy emitted when the one reacts with oxygen is of a quality readily absorbed by the other, the two acting in resonance." Now, if observation No. 4 (see above) be considered in connexion with this, it seems highly probable that the exact similarity in configuration of the carbon and positive nitrogen atoms in the two gases, combined with the fact that each molecule contains the same number of external as well as internal electrons (observation 5), may account for the two vibrating concurrently, *i.e.*, the similarity in structure accounts for the similarity in resonance effects. The hydrogen molecule, having an entirely different configuration from that of CO or nitrogen, would inhibit such concurrent vibration.

Referring to their statement that "This energy absorbing effect in nitrogen is far beyond that of all other di-atomic gases"; if the structures be worked out on the lines given above, no other di-atomic gas, with the possible exception of cyanogen, will be found to have a configuration anything like

that of either CO or nitrogen, and even cyanogen, the nearest to them, has 9 electrons in the combined octets of its molecule, whereas CO and nitrogen have 10 each.

This arrangement of the nitrogen molecule is the nearest approach to a sphere which can be obtained with the octets of the two atoms, which agrees with the calculations of Rankine (*Proc. Roy. Soc.*, 1921, A. 98, 360, 369, 331) of the atomic and molecular diameters, obtained from the viscosities.

The oxides of nitrogen will be represented as follows:—Nitrous oxide,  $\text{N}\equiv\text{N}=\text{O}$  in Fig. 3.

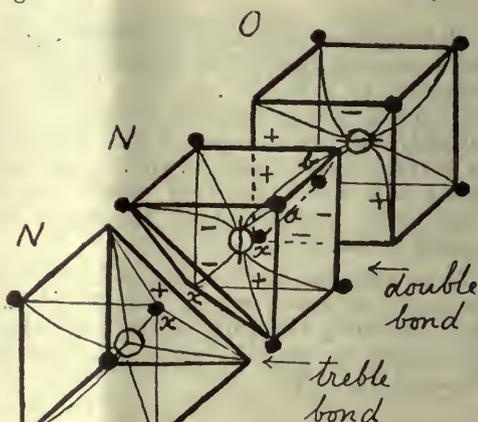
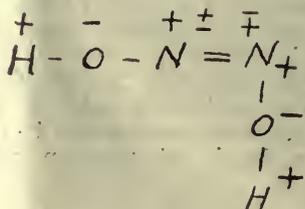


Fig. 3.

This formula gives a better explanation than any other of the ready formation of the nitrogen molecule when oxygen is abstracted from  $\text{N}_2\text{O}$ ; all that will happen after the oxygen has left the molecule is that the electron from (a) will travel to (b), and the cube corner at (a) will vanish, leaving a triangle and thus reforming the nitrogen molecule.

A further argument in its favour is that  $\text{N}_2\text{O}$ , which might be looked upon as the anhydride of hyponitrous acid, does not unite with water to form that acid, since water is not a strong enough reagent to rupture the treble bond and open up the nitrogen octets, whereas in the decomposition of hyponitrous acid



to  $N_2O$  and water, the treble bond might be easily reformed from the double bond.

It is also in agreement with Rankine's calculations (*loc. cit.*), in which he finds that  $CO_2$  and  $N_2O$  molecules are similar in size and shape, which can be seen by comparing this formula with that given for  $CO_2$  in Part III. It will also be noticed that the two gases have the same number of external electrons in their molecules.

It presents no free valencies in the nitrogen atoms which precludes the easy addition of oxygen to form higher oxides. As thus constituted, there are two weaknesses in the  $N_2O$  molecule.

(1) In the pentavalent nitrogen atom, both positive and negative bonds come into play (rule 2).

(2) The corner at  $x$  (fig. 3), which is shared by all three atoms, will be occupied by two electrons (rule 6).

The oxygen atom is, for these reasons, easily detached from the rest of the molecule.

Nitric oxide  $N=O$  in Fig. 4.

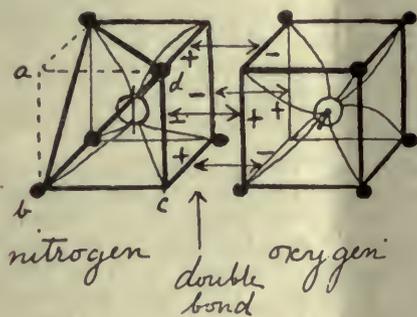


Fig. 4

(To be continued.)

### SOME RECENT RESEARCHES IN ORGANIC CHEMISTRY.

By R. F. HUNTER, F.C.S.

Researches in the field of Organic Chemistry, have increased during the last few years in such number and magnitude that a mention of a few of the problems, and it can be little more than a mention which our leading researchers and pupils have been attacking, would not seem out of place. Since those of us who are academic researchers and whose duty it is, therefore, to keep pace with the enormous

work which is being done, are finding it increasingly difficult to keep pace with new developments, we fear that the industrial chemists amongst us must, in the main, have given up (save where their own specialised branches are touched on) as a hopeless task the attempt to keep pace with the researches carried out in the laboratories of our Universities. This being so, a series of articles on the subject should not be out of place. One point necessary to mention is this—the brilliant work which has been carried out in the laboratories of the Royal College of Science during the last ten years or so under the guidance of Prof. J. F. Thorpe and Dr. C. K. Ingold on Dynamic Tautomerism, Stability of Spiro Compounds, etc., has not been included, for the reason that it will be dealt with much more fully at a later date. The researches with which we propose to deal are those which have taken place during the last three years or so, that is to say, we do not propose to go further back than 1920, and further to confine attention on the work done in this country.

The greatest difficulty is obviously to separate the most vital considerations from the hosts of other important considerations, and in the present state of knowledge and the extreme recent date of the work this becomes difficult. This being so, it will not be thought necessary if less important problems, since they will only be shown to be of lesser importance at a later date, are given more consideration than more vital problems. In composing this piece of work, the material has, largely, been based upon the accounts given in the *Chemical Society's Journal*, where full experimental details and foreign references can be found.

An interesting preparation, that of chlorpicerin from picric acid and tri nitro toluenes, was investigated by Orton and McKie. They prepared chlorpicerin by dissolving picric acid in sodium carbonate to give the sodium salt, obtained a paste, and acted on this with chlorine at  $5^{\circ}C$ . They examined the solubility of chlorpicerin in water, and also investigated the action of a hypochlorite solution on

o & p Nitro phenol,  
2:4 Dinitrophenol,  
and Trinitro toluene and tri nitro toluene residues.

The research was communicated to the Chemical Society in November, 1920.

The same month, Chattaway and Ray

studied the old familiar problem of the decomposition of tartaric acid by heat.

Tri thio carbonate and per-thiocarbonates were investigated by Yeoman at this time. Among the problems studied were the method of analysis, the compound sodium tri thio carbonate and the corresponding potassium, calcium, barium, strontium and ammonium salts. About this time the first part of Henstock's work on the bromine compounds of phenanthrene appeared. Briefly we can say that he prepared compounds which appear to be, and which he headed as

- 2 (?) Bromophenanthrene Dibromide,
- 2 (?) 10 Dibromophenanthrene,
- 2 (?) 10 Dibromophenanthrene,
- 2 (?) 10 Dibrom 9 nitro phenanthrene,
- 2 (?) 10 Dibromo 9 amino phenanthrene,
- 10 Bromo 2 ethoxy phenanthrene, and
- 9:10 Dinitro 2 ethoxy phenanthrene.

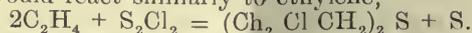
In the next month, McKenzie and Barrow published a paper on  $\beta$  amino,  $\beta$  phenylpropic phenone, this being the result of the fact that for another research it was desired to obtain a  $\beta$  amino ketone containing an asymmetric carbon atom.

In the experimental work, we have the preparation of  $\beta$  amino  $\beta$  phenyl propionic acid from cinnamic acid and hydroxylamine and the study of the action of  $\beta$  formylamino  $\beta$  phenyl propionyl chloride on benzene in the presence of aluminium chloride, the action of cinnamoyl chloride on benzene under the same conditions. Also the preparations of

- $\beta$  Benzoylamino  $\beta$  phenyl propiophenone,
- $\beta$  Phthalimino  $\beta$  phenylpropionic acid,
- $\beta$  Phthalimino  $\beta$  phenyl propiophenone,
- $\beta$  Benzoyl and phenyl ethyl phthalamic acid, and

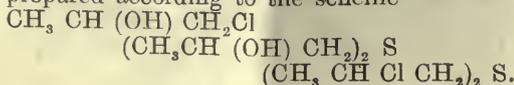
$\beta$  Amino  $\beta$  phenyl propiophenone.

About this time a communication of Coffey's appeared on the action of sulphur chlorides on substituted ethylenes, the action of propylene on sulphur monochloride and the synthesis of  $\beta\beta'$  "Dichloride n propyl sulphide, one of the many researches entailed by the production of mustard gas  $\beta\beta'$  "dichlorethyl sulphide for war purposes. It was considered that propylene would react similarly to ethylene,



A small quantity of  $\beta\beta''$  'dichloride n propyl disulphide was isolated.

$\beta\beta''$  'dichloride di n propyl sulphide was prepared according to the scheme



The oxidation of  $\beta\beta'$  dichloride n propyl sulphide by nitric acid was also investigated.

Brady and Gibson communicated from Woolwich Arsenal the results of a research upon

2 : 4 : 6 Tri nitro tolyl methyl nitroamine.

The preparation of a number of related compounds were incidentally discussed.

Arylazoglyoxaline carboxylic acids were studied by Fargher about this time, the work mainly experimental, and among the preparations were 4-p-Bromobenzeneazo 2-phenyl glyoxaline-5-carboxylic acid 4-p-Bromobenzeneazo 2-methylglyoxaline-5-carboxylic acid 2-p-Bromobenzeneazoglyoxaline 4 : 5-dicarboxylic acid.

Meanwhile Nierenstein published the third part of the research on the constitution of catechin and the synthesis of acatechin. The communication contained the synthesis of 2 : 4 : 6 : 3' : 4'-penta-hydroxy-3-phenylchroman. This was obtained by the following method:—3 : 4 : 2' : 4' : 6'-penta-methoxy-diphenylmethylchloromethyl ketone was converted into 4 : 6 : 3' : 4' tetramethoxy-3-phenylchroman-2-one, this reduced to 2-hydroxy-4 : 6 : 3' : 4'-tetra-methoxy-3-phenylchroman, and this, on demethylation, gave the required 2:4:6:3':4'-penta-hydroxy-3-phenylchroman.

Morgan and Vining studied in some detail the subject of Dihydroxy naphthaldehydes. Among the general preparations were those of Dihydroxy naphthaldehydes and their p Bromo phenylhydrazones,  $C_6H_4BrNHN : CH C_{10}H_5(OH)_2$ , Dihydroxy naphthylideneanilines,  $C_6H_5N : CH C_{10}H_5(OH)_2$ .

A paper of Morgan and Jones appeared on ortho Chlorodinitro toluenes, and among the questions studied were:

- Nitration of 2 Chloro 6 nitro toluene;
- Action of diazonium salts on 6 Chloro;
- 2 : 4 tolylenediamines.

The action of primary amines on 4 : 5 and 5 : 6 dinitro o chlorotoluenes.

In January, 1921, a number of papers on organic research were communicated to the J.C.S., these were briefly as follows:—

The constitution of Disaccharides, Pt. V., Cellobiose, by Haworth & Hirst, which consisted essentially of the preparation of cellobiose, octa acetate, the methylation of cellobiose, isolation of heptamethyl methyl cellobiose, the hydrolysis of heptamethyl methyl cellobiose, and the conversion of crystalline tri methyl glucose into tetramethyl glucose.

Derivatives of Gallic Acid, Pt. II., by

Meldrum, appeared, in which condensations of gallic acid were examined. In the experimental work there appeared

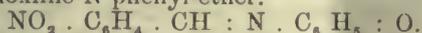
3 : 4 : 5-Tri-hydroxy-2-tri-chloromethyl phthalide.

The lactone of 7 : 8 dihydroxy 2 : 4 bis tri-chloro-methyl-6- $\beta$ -trichloro -  $\alpha$ -hydroxy-ethyl 1 : 3-benzdioxine-5-carboxylic acid.

The lactone of 7 : 8  $\beta\beta\beta$ -trichloroethylidene dioxy 2 : 4 bis tri chloro methyl 6  $\beta\beta\beta$ -tri-chloro  $\alpha$  hydroxyethyl-1 : 3-benzdioxine-5-carboxylic acid. 6-Methyl-2 : 4-bis-tri-chloromethyl-1 : 3-benzdioxine - 8 - carboxylic acid. 4 Hydroxy 5  $\beta\beta$  dichloromethyl-m-toluic acid. 6 Hydroxy 5 carboxy-m-tolylacetic acid, and  $\beta\beta\beta$ -trichloro 4 : 4' dihydroxy  $\alpha$  a di-m-tolyethane-5 : 5'-dicarboxylic acid.

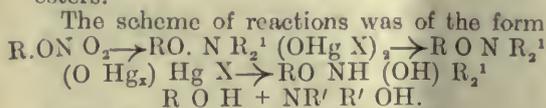
A short paper by Singh and Lai appeared on substituted Quaternary Azonium compounds, which contain an asymmetric carbon atom.

The work of Barrow and Griffiths on the condensation of p-nitro-benzyl-chloride with nitroso compounds, which contained a new mode of formation of N Oximino ethers, appeared, the experimental part of which contained the study of p-nitro-benzaldoxime-N-phenyl-ether.



Perkins and Tucker's research on the oxidation of carbazole appeared about this time. In the experimental portion, we have the oxidation of carbazole by permanganate of potash in acetone solution. From the reaction two isomeric dicarbazyls were isolated, both of formula  $\text{C}_{24}\text{H}_{16}\text{N}_2$ , a third amorphous product of oxidation was isolated. All three substances were found to be capable of nitration, bromination, and to react under certain conditions with acetic anhydride.

Towards the end of December, 1920, Hepworth communicated an investigation on the action of Grignard reagent on nitro esters.



Among the preparations were:

Dimethyl hydroxylamine hydrochloride and oxalate, and the reactions studied were those of

Mg MeI on ethyl nitrate, Mg Et Br on ethyl nitrate, Mg Br Et on ethylene glycol dinitrate. Mg MeI and Mg Br Et on nitroglycerin and pentaerythritol tetranitrate.

Crossley and Renvuf contributed a paper on 1 : 1 dimethyl cyclohexane from hep-

tenone, the research was mainly on Kelnisky's previous work. At the same time there appeared another paper by Nierenstein on Gallotannin. The work was mainly quantitative, and essentially consisted of quantitative observations on production of Ellagic acid from gallotannin and several gallotannin residues were studied.

(To be continued.)

## THE BRITISH EMPIRE EXHIBITION (1924).

The Editors of the various technical journals met Mr. Woolcock, the General Manager of the Association of British Chemical Manufacturers, at the offices of the Association in Piccadilly, to discuss with him the progress which has been made with the preparation of the Chemical Section. In the course of the conversation, Mr. Woolcock said:—

"The Chemical Section which is being organised by the Association, and occupies nearly 40,000 square feet in the Palace of Industry, will be built in such a way as to form a hall within the palace. About one hundred thousand pounds will be spent in presenting to the public a picture of the present state of British Chemical Industry. No important firm in the industry will be unrepresented, and the whole of the individual exhibits, numbering about one hundred, will, by reason of their position and character, combine to form a magnificent illustration of the industry. The treatment of the individual stands is being done on lines which have never before been attempted, and the old and somewhat hideous structures which have disfigured exhibitions in the past will not appear. Considerable attention has been paid to the lay-out and to the decoration of the Chemical Hall. There will, for example, be about two hundred yards of a specially painted frieze, illustrating various operations in chemical manufacture, and as the majority of the stands are being designed by the same architect, the treatment of each stand is likely, while maintaining the individuality of the occupier, to present a very pleasing picture of the hall as a whole. It has not, however, been considered sufficient that we should merely show visitors examples of the products of the industry. The best possible exhibition of this kind would leave one question unanswered. The visitor may be satisfied that he is witnessing a demonstra-

tion of the position to which the industry has attained, but what the critical person who examines the exhibit requires to know is whether there is behind this example of what has been achieved a scientific basis which will ensure the continuance of this progress. For this reason, in the centre of the Chemical Hall, there is to be illustrated the progress which has been made in pure chemistry during the past twenty or thirty years, with a view to showing that the stream of scientific invention in this country is still flowing steadily onwards."

Mr. Woolcock then proceeded to outline the scheme of classification which has been adopted for the Scientific Section, and enumerated a number of names of those scientists who have already promised their assistance, and very few of the outstanding scientific men of the day were absent from the list. Continuing, Mr. Woolcock said: "The Scientific Section is being organised by a Committee consisting of representatives of the following bodies:—

The Chemical Society.

The Institute of Chemistry.

The Society of Chemical Industry.

The Society of Dyers & Colourists.

The Pharmaceutical Society.

The Institution of Petroleum Technologists.

The Institution of Chemical Engineers.

The Committee is working in close co-operation with the Royal Society. Sir Herbert Jackson acts as the representative of the Royal Society on the Committee, and myself in a similar capacity on the Royal Society Committee. In this way we shall prevent any overlapping. In order that both the general public and scientific persons may have a record of the exhibit, it is proposed to publish a number of pamphlets (specially written for the purpose) dealing in popular language with the various classes of exhibits in the Scientific Section. In addition to this it is proposed to publish in more technical language a work, which will not only explain the scientific exhibits, but which will put on record in a very complete form the state of our knowledge in chemical matters at the date of the Exhibition. It is anticipated that there will be a very large demand for this valuable record, and that it is likely to find a place on the bookshelf of every scientist. The various chapters will be written by the acknowledged experts in their subjects, and I anticipate that the contents of this book will be very valuable matter for reference."

Mr. Woolcock invited the assistance of

the Editors in making widely known what was being prepared for the Exhibition next year, and the following resolution was unanimously passed:—

"That our best thanks be extended to Mr. Woolcock for his courtesy in inviting the Editors of the trade and technical press to meet him, and that we undertake to give him any assistance in our power in organising the publicity service of the Chemistry Section."

### ANHYDROUS ALUMINUM CHLORIDE.

[Abstracted from Technical Paper 321, By OLIVER C. RALSTON, issued by the U.S. Dept. of the Interior, Bureau of Mines.]

Anhydrous aluminum chloride is a pure white microcrystalline solid which is usually yellow to brown, or bluish to greenish, due to the presence of impurities, especially iron. When heated, it sublimes with only a hint of fusion and the temperature of sublimation—between 181° and 195° C.—is somewhat difficult to measure. Under a pressure of about 2.5 atmospheres, it can be melted at 194° C. Its boiling point at atmospheric pressure is thought to be about 179° C. When condensed, the ruling temperature in the condenser is about 181° C.

Aluminum chloride is extremely hygroscopic, absorbing moisture from the air to form aluminium oxide ( $Al_2O_3$ ) and hydrogen chloride (HCl); the smell of the latter is always noticeable whenever a container of aluminium chloride is opened. This reaction between moisture and aluminum chloride often does not take place at once, but the hydrochloric acid is given off slowly on standing. If the surface of a mass of anhydrous aluminum chloride is allowed to "glaze" with a coating of aluminum chloride hydrate ( $AlCl_3 \cdot 6H_2O$ ) and the mass is then sealed in a tight container, the water of the hydrate slowly diffuses to the remaining anhydrous material and reacts to form aluminum oxide and hydrochloric acid gas. As the reaction proceeds the pressure of the gas finally becomes strong enough to burst the container. A glass bottle filled with aluminum chloride which has been exposed to the open air for a few minutes before being placed in the bottle may blow its stopper in this way. Large drums filled with the commercial product have been

known to "explode," probably from this cause.

This chloride is completely soluble in a large excess of water, with no visible hydrolysis; it dissolves with a hiss and with the generation of heat. Aluminum chloride is also easily soluble in alcohol, ether, and liquid chlorine, and dissolves quickly in dry petroleum products, producing a brown to black coloration. Sample bottles containing anhydrous aluminum chloride should not be sealed with paraffin, as the salt will turn it black. The solution of aluminum chloride in a petroleum product may segregate into two layers on standing, with the aluminum chloride dissolved in the highly coloured lower layer. On heating, this layer mixes with the one above. No tests have been made to see if a small amount of aluminum chloride is also contained in the upper layer. Aluminum chloride is much more soluble in warm than in cold oils; in fact, at the petroleum refineries it is dissolved in warm oil and piped to the stills, where it is used as a catalyzer.

In the fused condition anhydrous aluminum chloride mixes with sodium chloride in all proportions. The double compound,  $\text{AlCl}_3\text{-NaCl}$ , is supposed to exist and to have a melting point of  $185^\circ\text{C}$ . It has been obtained by volatilising a mixture of salt, alumina, and carbon by treatment with chlorine. The writer has not made a quantitative study of the system  $\text{NaCl-AlCl}_3$ , but has prepared mixtures of the two which were completely fluid at a temperature as low as  $136^\circ\text{C}$ . A eutectic between the double compound and aluminum chloride probably melts at about this temperature. The double compound formed the basis of the early aluminum industry; it was the bath from which aluminum was deposited by metallic sodium, until the present cryolite-alumina electrolytic bath displaced it.

The first large-scale use of aluminum chloride was in the preparation of aluminum metal by the reaction of sodium metal on the fused double aluminum-sodium chloride. At first, pure anhydrous aluminum chloride was made and added to the bath as the latter became depleted in aluminum; later, it was found much more convenient to prepare the double compound, which was more stable in air, not so hygroscopic, and could be melted and cast into blocks or rods ready to drop into the bath.

Anhydrous aluminum chloride is also used on a large scale in carrying out Friedel-Crafts organic reactions. The aluminum

chloride acts as a catalyst, causing the combination of two materials that would otherwise be indifferent to each other. In the manufacture of many dyes, perfumes, drugs, and pharmaceuticals a catalyzer is used at some point in the process. Aluminum chloride is classed more or less with zinc chloride as a "condensing agent" for organic chemical work.

Aluminum chloride is also being considered for the bleaching of brick, as red brick can be bleached to buff if iron is replaced by aluminum. Some steel companies have claimed, moreover, that the chloride could be used in removing certain impurities from molten metal. Any of the uses mentioned might develop on a larger scale if a cheap product could be produced.

The refining of petroleum, however, uses the largest amount of aluminum chloride at present, and seems likely to demand additional supplies of the chloride in the future. This salt seems to fulfil several major functions in the treatment of petroleum products.

First, it converts all unsaturated compounds. Frequently this conversion is made by throwing out the excess of carbon over hydrogen in the hydrocarbon, whereupon the carbon blackens the aluminum chloride and forms a coke; gases need not be liberated. The most astonishing consequence of this saturating action is that unstable gasoline and lubricating oils made from asphalt-base petroleum yield excellent stable products of good colour and odour; in fact, they are almost paraffin-base products.

The second main effect obtained by boiling petroleum products in the presence of aluminum chloride is a cracking action. High-boiling hydrocarbons can be converted into low-boiling hydrocarbons, with the formation of some coke and some fixed gases as by-products. A topped oil, a gas oil, or a fuel oil can be treated with aluminum chloride catalyzer in a simple boiling still at atmospheric pressure with a yield of 60 to 85 per cent. of low-boiling oil containing fractions of petroleum ether, gasoline, and kerosene. The residue is coke containing the aluminum chloride, and can be used over several times before it becomes exhausted by the aluminum chloride losing its activity. Possibly the aluminum chloride is buried in the carbon or combines with it. The distillates are all saturated sweet-smelling products.

If desired, the distillation need not be

carried completely to coke, but can be stopped, and some excellent lubricants will be found in the heavier fractions remaining. Because of the volatility of aluminum chloride, a reflux must be used to catch its vapours and return them to the still with any condensed hydrocarbons. This means that nothing heavier than kerosene can get past the reflux. If desired, the reflux can have its temperature so adjusted that nothing but gasoline and lower boiling hydrocarbons can get past it into the condenser. If the boiling is continued, everything in the still is cracked into gasoline, gas, and coke. The amount of coke remaining in the still is a fraction of the percentage of carbon originally present in the raw hydrocarbons treated.

A third function of aluminum chloride in petroleum refining is to remove sulphur from the oil. Part of the sulphur is converted into hydrogen sulphide gas and possibly aluminum sulphide is formed. At any rate, aluminum chloride is a very efficient desulphurizer. The desulphurizing uses up aluminum chloride, and for high-sulphur oils a correspondingly larger amount of aluminum chloride is needed. Consequently, to make the process commercially feasible, only a very cheap product can be used for removing sulphur, and enough of an excess must be added so that there will be free aluminum chloride to act as catalyzer for the saturating and cracking.

#### METHODS OF PRODUCING ANHYDROUS ALUMINUM CHLORIDE.

Oersted, who first prepared aluminum chloride, passed a current of dry chlorine over a heated mixture of carbon and alumina. This method was afterwards used by Wöhler (1827), Leibig (1830), Bunsen (1854), and Deville (1849). Deville was one of the fathers of commercial aluminum metal, and used aluminum chloride as the raw material from which to extract it. The following methods of producing aluminum chloride are not grouped chronologically, but rather by relative importance in present manufacture. Those near the end of the list are largely processes collated from patent literature or elsewhere.

1. Dry chlorine gas acting on aluminum metal.
2. Dry hydrochloric acid gas acting on aluminum metal.
3. Chlorine gas acting on mixtures of aluminiferous and carbonaceous materials.
4. Chlorine gas or hydrogen chloride acting on aluminum carbide.

5. Chlorine gas acting on aluminum nitride.

6. Chlorine gas and carbon disulphide vapour acting on aluminiferous materials.

7. Chlorine compounds of carbon acting on aluminiferous materials.

8. Chlorine compounds of sulphur or arsenic acting on aluminiferous materials.

9. Dry lead chloride reacting with aluminum metal or with aluminum carbide.

10. Anhydrous calcium chloride reacting with aluminiferous materials.

11. Aluminum chloride solutions prepared by any wet method, then evaporated and the crystals dehydrated.

All of these methods, with the exception of method 11, are performed at high temperatures, usually high enough to sublime any aluminum chloride formed. In fact, the great volatility of aluminum chloride is frequently the main inducement to reaction and many of the above processes are endothermic. Details of each of these groups of methods are discussed on the following pages.

#### THE EVOLUTION OF CHEMICAL TERMINOLOGY.\*

By JAMES F. COUCH.

(Continued from Page 238.)

"A compound of an element or radical with hydrogen and oxygen, not regarded as containing water. . . . The term is usually applied, and by many chemists restricted, to compounds containing the group OH, or hydroxyl. Hydroxides may be basic, neutral, or acid, according to the nature of the combining atom or radical. Most hydroxides, commonly so called, however, are basic." p. 1055.

On April 20 of this year *Science*\* published a list of rules adopted by the Nomenclature Committee of the American Chemical Society and that of the London Chemical Society, in which the following appears:

"The word *hydroxide* should be used for a compound with OH and *hydrate* for a compound with H<sub>2</sub>O. Thus, barium hydroxide, Ba (OH)<sub>2</sub>; chlorine hydrate, Cl<sub>2</sub> 10 H<sub>2</sub>O."

Murray<sup>36</sup> defines hydroxide as:

\* *Science*, N.S. 57, 474 (1923).

\* [Reprinted from "*The American Journal of Pharmacy*, Philadelphia, Pa., July, 1923.]



"A compound of an element or radical with oxygen and hydrogen, not with water; by some chemists restricted to compounds whose reactions indicate the presence of the group hydroxyl (OH)." p. 491, v. 5.

Mellor<sup>32 33</sup> extends the term to all hydroxyl compounds but recognises that it is used in the narrower sense where it applies only to basic compounds. In this modified view he is in accord with Silliman.<sup>46</sup> He says:<sup>32</sup>

"From this point of view water can be regarded as hydrogen hydroxide, H-OH, analogous with K-OH, potassium hydroxide, and Na-OH, sodium hydroxide. Excluding certain carbon compounds, the hydroxides of the non-metallic elements are usually acids, and the hydroxides of the metals are usually bases. The term 'hydroxide' is generally reserved for compounds of the basic oxides with water; and the term 'anhydride' is usually reserved for the acid anhydrides." p. 146.

The same idea is repeated in his great "Comprehensive Treatise,"<sup>33</sup> and here he insists upon the broadest extension of the term in theory:

"Every element, excepting fluorine and the argon family, appears to form one or more hydroxides, directly or indirectly." v. 1, p. 395.

Sharply contrasted with these views is that concept of the term hydroxide which to-day is held by the great majority of chemists, the limitation of the term to those hydroxyl compounds which exhibit basic properties. As I shall show, this view is the original idea expressed by the term, and has been held continuously, although obscured and distorted by changing notions of chemical theory, during the past twelve decades. Williamson<sup>35</sup> in 1851 wrote:

"The experiments of M. Chancel, agreeing in result with my own, have clearly proved that the numerous family designated as hydrated oxides are formed by the juxtaposition of an atom of water with an atom of metallic oxide, e.g.,  $K_2O + H_2O$ , but that the equivalent of the molecule is half that quantity.

H

namely — O; they are not compounds of K

water but products of substitution in water . . . alcohols, which are truly hydrated oxides, must be considered as products of substitution of the compound radicals, . . . for half the hydrogen of water."

At that time the compound radicals, or, as we should to-day term them, the alkyl radicals, and the alcohols as well, were considered basic in nature. This work of Williamson first brings out clearly the idea of hydroxyl compounds.

Roscoe<sup>44</sup> in 1873 definitely limits the application of the term:

"Viele basische Oxide verbinden sich mit Wasser zu einem Hydroxide." p. 153.

"Die im Wasser löslichen Hydroxide haben, wie schon früher erwähnt, eine alkalische Reaction." p. 154.

Kolbe<sup>30</sup> concurs in this view:

"The name hydrate includes two classes of bodies; the acid hydrates (the oxy- or sulpho-acids) and the basic hydrates (the hydrates proper)." p. 56.

Nuttall<sup>38</sup> is admirably definite:

"Hydroxide, a metallic hydrate." p. 185.

Richter<sup>43</sup> meets the issue squarely also:

"Some of the elements yield acids by their union with oxygen, or more correctly oxides, which form acids with water. Most of these are the metalloids. . . .

With oxygen the metals usually yield oxides, which form hydroxides (hydrates) or bases with water." p. 84.

The "Century Dictionary"<sup>41</sup> supports this view:

"A metallic or basic radical combined with one or more hydroxyl groups, as potassium hydroxide, KOH; ethyl hydroxide,  $C_2H_5OH$ . Hydroxides may be regarded as formed from water (HOH) by the substitution for one of its hydrogen atoms of a metal or basic radical. An acid radical combined with hydroxyl is called an acid, the term hydroxide being reserved for basic compounds." v. 5, p. 2940.

The following quotations are taken from the fourth edition of Roscoe and Schorlemmer's "Treatise on Chemistry":<sup>45</sup>

"The acid-forming oxides combine with water to form hydrates which are termed acids." p. 261, v. 1.

"The basic oxides . . . form in combination with water a class of compounds termed hydroxides or hydrated oxides. . . ." p. 260, v. 1.

These quotations show that since the middle of the last century there have been extant and co-existent three well-defined and distinct concepts of the term hydroxide and that these three views persist to the present time, particularly in textbooks. In order to reach a decision as to which of these three definitions we should accept and which discard, let us consider the historical

development of the term. In the course of this investigation we shall find it necessary to go back to the very beginning of modern chemical nomenclature and to examine the works of those men who laid the foundations of our science.

The word oxide was coined by a French chemist, de Morveau,<sup>34</sup> in 1787. This man of genius and insight formulated the first scientific system of chemical nomenclature with Lavoisier, Bertholet, and de Fourcroy. He was specific in his definition of the word oxide, and the meaning he gave it was generally accepted until the downfall of Berzelius' electro-chemical theory, when chemical theory was thrown into a state of flux, and the term oxide was extended to include the oxygen compounds of the non-metals. De Morveau says:

"Nous avons donc dû chercher une expression nouvelle, & pour la rendre conséquent à nos principes, nous avons formé le mot *oxide*, qui d'une part rappelle la substance avec laquelle le métal est uni; qui d'autre part annonce suffisamment que cette combinaison de l'oxygène ne doit pas être confondu avec la combinaison acide, quoiqu'elle s'en rapproche à plusieurs égards." p. 56.

"Après avoir établi la distinction des acides & des oxides métalliques, c'est-à-dire des métaux oxygène & des métaux simplement oxidés." p. 58.

The acids are not oxides, according to this statement, but are compounds of oxygen with acid-forming elements. This curious distinction is based upon a difference in function of the resulting compounds and shows clearly the insight of the man in not confounding a similarity in process of preparation with a systematic likeness.

The next event of interest in development of the word hydroxide occurred twelve years after the coining of the term oxide. In 1800 Joseph Louis Proust\* devised the word hydrate and applied it to the hydroxides of copper.

"Le second est une combinaison particulière de l'oxide et d'une quantité fixe d'eau concrète, d'où dépend sa couleur, et que j'ai crû devoir nommer *hydrate de cuivre*." p. 41.

Proust's concept of hydrates is identical with the most limited modern view of hydroxides. Contemporaneous chemists accepted the term and used it in this sense ex-

clusively. The use of hydrate in place of hydroxide still persists at the present time, particularly in England, where the term was readily accepted. Proust had definite ideas about the hydrates; he felt that they were true compounds and, in defending this view, entered into that brilliant controversy with Bertholet which eventually firmly established the law of definite proportions. Proust says:

"100 parties d'hydrate distillés donnent 24 parties d'eau, 75 d'oxide noir (of copper), et la valeur d'un grain d'acide carbonique, étranger à cette combinaison, et qui s'y trouve par des causes que nous éclaircirons tout à l'heure." p. 43.

"Dans l'hydrate de cuivre récent, il ne peut exister aucun soupçon d'acide." p. 43.

He subsequently developed the idea, and applied the term to other metallic hydroxides.<sup>40 41</sup> In 1804, in answer to objections, he retorts that in the hydrates the water acts the part of an acid (p. 348), thus anticipating, by eight years, Berzelius, who is generally considered the father of that idea. His notions are well displayed in the following statements:

"L'hydrate est, comme j'en ai fait voir antérieurement, la combinaison d'un oxide avec l'eau." " . . . je n'hésiterai point à assurer qu'il y a non-seulement des hydrates métalliques, mais même aussi des hydrates alcalines et terreux."

"On ne peut nier aujourd'hui que la chaux ne se combine avec l'eau." p. 347.

Smithson,<sup>47</sup> reporting the analysis of some calamines, uses the term hydrate in accordance with the ideas of Proust:

" . . . it seems to consist of two matters; carbonate of zinc, and a peculiar compound of zinc and water, which may be named *hydrate of zinc*." p. 22.

Klaproth and Wolff<sup>28</sup> in 1810 reflect the definite concept of the term:

"Proust first gave the name of hydrate to the combinations of metallic oxides with water." v. 2, p. 518.

John Davy<sup>14</sup> in 1811 refers to "hydrate" of potash, and Vogel<sup>49</sup> uses hydrate, both of them in the limited sense that Proust imposed upon the word. Humphry Davy<sup>12 13</sup> did not accept the term, apparently, for he makes no use of it.

The first use of the term hydroxide eluded our search for months. It is evident that it could not have preceded the coining of

\* "Recherches sur le cuivre," *Ann. de Chim.*, 1800, 32, 26-54.

the word oxide, which occurred in 1787, so with that as a lower limit a search of the literature was initiated which involved the scrutiny of every publication which might conceivably include the word. Cutbush<sup>9</sup> defined the term in 1821, and it was used by Henry<sup>25</sup> in 1823. Then it totally disappears from the literature until 1851, when it reappears in the "Catalogue of the Great Exhibition."<sup>3</sup> It is not used by Kels,<sup>27</sup> Chaptal,<sup>5</sup> Davy,<sup>12 13</sup> Dalton,<sup>10</sup> Silliman,<sup>46</sup> Cutbush in 1814,<sup>8</sup> Hare,<sup>24</sup> Gay Lussac,<sup>18 19</sup> d'Aubuisson,<sup>1</sup> Vogel,<sup>49</sup> or Berzelius.<sup>2</sup> These papers cover a period of forty-two years, from 1791 to 1833, and, had the term been in wide use, would undoubtedly have included it.

The word hydroxide was coined in 1802 by Richard Chenevix,<sup>6</sup> who proposed it as a better form than Proust's hydrate, against which Chenevix urged some objections. He says:

"Hydro-oxide had been a much more proper appellation, as it would express the combination not of Hydrogen, but of water; which is the truth." p. 34.

"I have stated before that Hydro-oxide, or Hydroxide, would be the proper term for all combinations of metallic oxides with water; for such combinations as Copper, Cobalt, Nickel, and Uranium are capable of affording." p. 77.

A word concerning this man, now almost forgotten in science, who coined so widely used a term, may not be out of place here. Chenevix was born in Dublin, Ireland, in 1774, and died in Paris in 1830. When twenty-four years of age he published his first paper on a chemical subject, and for ten years was active in chemistry, publishing twenty-four papers in all until 1808, when he suddenly disappears from scientific literature. In the latter part of his life he was a successful dramatist and novelist.

He evidently did not possess sufficient personal influence to supplant Proust's hydrate with his term, for to the prestige of the professor at Madrid alone can we attribute the long survival of the former term. It was not until a great development in chemical theory and a fundamental change in point of view demanded a revision of our notions of the mechanism of water-combinations that the term hydroxide was firmly established in chemical terminology. Watts,<sup>8</sup> in 1864, and his third supplement, published as late as 1881, do not mention the term. From the start, however, an exemplary definiteness of meaning was attached to the term. Witness Cutbush:<sup>9</sup>

"Hydro-oxides. Oxydes combined with water." p. 31.

"Hydro-oxides. Oxydes combined with water." p. 31.

"Hydrate. A chemical combination of a body with water." p. 29.

"Oxydes. Combinations of oxygen with different bases, not possessing, strictly speaking, acid properties." p. 49.

"Sulphuric acid. . . . A compound of sulphur and oxygen." p. 73. and Henry:<sup>25</sup>

"The compounds of (metallic) oxides and water in which the latter exists in a condensed state, are termed hydrates, or hydro-oxides, or hydroxures." v. 2, p. 42.

In 1851,<sup>3</sup> after a disappearance of nearly thirty years from the literature, it still is used only for basic compounds:

"The whole coast of Andalusia is rich in galenas; the province of Malaga yields this product mixed with pyritic iron and hydroxidated iron, at Mijar." p. 1326.

"13. Hydroxide of iron, from San Claudio." p. 1327. ". . . enveloping the bunches of hydroxide of iron." p. 1328.

These quotations make it clear that, in their original meaning, both of the terms, hydroxide and hydrate, connoted compounds of basic oxides with water or what we should to-day refer to as basic hydroxides. The original meaning of the word acid is clear, the oxygen compound which (dissolved in water) possesses acid properties. An acid is not an oxide, de Mourveau,<sup>34</sup> Cutbush,<sup>9</sup> and Hare.<sup>24</sup> The latter says:

"All the binary combinations of oxygen have been called oxides, when not acid." p. 209.

The correlative term base is equally clear. Cutbush defines it:

"Base A term used to express the earth, alkali, or metal, which forms a salt with an acid." p. 12.

The work of Williamson<sup>53</sup> made necessary some stated distinction between classes of compounds in which water exists as such and in which it exists in a rearranged form. The term hydrate was convenient and, although it had been applied by Proust and his contemporaries specifically to what we now term hydroxides, it had gradually been extended to include all compounds of water. Substances which contain water of crystallisation, hydrated compounds in which the water is patently present in something more than physical union, and even masses which were merely

moistened with hygroscopic water, were all sub-summed in the category hydrate. This state of affairs was not so serious while the Berzelian notions of chemical theory held the field, but, when the electro-chemical hypothesis was overthrown, the newer ideas demanded more definite conceptions of the character of water of hydration; more specific explanation of the way in which water is combined, and some way of distinguishing between compounds whose water may be readily driven off by heating and those which are unaltered by any heat or only by very high heat.

The hypotheses of acid water and basic water no longer were satisfactory; it was also evident that a great difference exists between water as combined in the alkaline hydroxides and as united in crystalline sodium sulphate. The term hydroxide began to be used again, but with rather indistinct meaning as denoting something in which water is combined more firmly than in the hydrates. Clarke<sup>7</sup> and Perkin<sup>29</sup> attempted to apply physico-chemical tests to compounds to establish a definite distinction between hydrates and hydroxides. The former determined the specific volumes of a large number of water-compounds, including hydrated salts and alkaline hydroxides. He found that the effect of combined water in the hydrated salts was nearly regular; that the mean value for the molecular volume of each molecule of water of crystallisation is 13.76, but that there is no such regularity observed in compounds in which, as we would now say, the hydroxyl group occurs. Perkin measured the magnetic rotatory power of many compounds and their hydrates, and came to the conclusion that if hydration increased the rotatory power by about unity the new compound is a hydrate.

The distinction between the two classes of compounds is, however, difficult to draw from such data and considerations. It is far simpler and more satisfactory to decide the question by analysis of the chemical relationships of the substance. Muir was led into the absurdity of deciding that cupric hydroxide is a hydrate, whereas arsenic acid ( $H_3AsO_4$ ) is an hydroxide<sup>35</sup> by failure to observe this principle.

This mass of evidence may be summarised thus: The terms hydrate and hydroxide were originally synonymous and were specifically applied to basic hydroxides. The acids were not classed as oxides and the chemistry of the alcohols, phenols, and carbohydrates had not been developed, so that there could be no inclusion of these com-

pounds in the concepts. The term acid was confined to those oxygen-compounds which united with bases to form salts, and this statement also defined bases as those substances whose combination with acids produced salts.

The original conceptions of hydrates and hydroxides persisted until well past the middle of the last century; the term hydrate being gradually used in a more inclusive sense until, finally, the necessity of discrimination among the compounds of water forced action and the result was a muddling of both notions which has come down to us at the present day and constitutes the problem of this paper.

I think that there will be general agreement to-day that hydroxides are not to be regarded as water compounds; that type of substances may be characterised by the term hydrate. The characteristic of an hydroxide, then, must be content of hydroxyl, and our definition of the term will depend upon the modifications and limitations which we impose upon this concept.

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<sup>52</sup> "New International Dictionary of the English Language," 1919.

(To be continued.)

#### GENERAL NOTES.

#### BOARD OF TRADE ANNOUNCEMENT.

##### DYESTUFFS (IMPORT REGULATION) ACT, 1920.

##### APPLICATIONS FOR LICENCES IN SEPTEMBER.

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during September, has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee.

The total number of applications received during the month was 457, of which 311 were from merchants or importers. To these should be added the 34 cases outstanding on the 1st September, making a total for the month of 491. These were dealt with as follows:—

Granted—341 (of which 300 were dealt with within 7 days of receipt).

Referred to British makers of similar products—79 (of which 65 were dealt with within 7 days of receipt).

Referred to Reparation supplies available—30 (all dealt with within 2 days of receipt).

Outstanding on 30th September, 1923

—40 (all dealt with at meeting of the Committee held on the 5th October).

Of the total of 491 applications received, 395 (or 80 per cent.) were dealt with within 7 days of receipt.

#### DYESTUFFS INDUSTRY DEVELOPMENT COMMITTEE.

The Board of Trade announce that they have appointed Dr. A. T. de Moulpiéd, of the British Dyestuffs Corporation, Ltd., to be a member of the Dyestuffs Industry Development Committee set up under Sub-section 2 (6) of the Dyestuffs (Import Regulation) Act, 1920, in the place of Dr. Herbert Levinstein, F.I.C., resigned.

#### REPORT OF OXYGEN RESEARCH COMMITTEE.

This Report\* describes certain aspects of the work of the Oxygen Research Committee since its appointment in 1919. It deals chiefly with the technical difficulties which have hitherto restricted the commercial utilisation of liquid oxygen and liquid air, and describes in particular recent improvements in the methods of handling the liquefied gases on a practical commercial scale. The work of the Committee has been carried out principally in the Heriot Watt College, Edinburgh, and the Air Ministry Oxygen Laboratory.

\* Published for the Department of Scientific and Industrial Research, by H.M. Stationery Office. Price 8s. 6d. net.

#### WIRELESS STATIONS IN RUSSIA.

A translation of a Decree of the Council of Peoples' Commissaries of the Union of Soviet Socialist Republics, dated July 4, and published in the "Izvestra" of September 12, regarding the installation of wireless stations by State, Trade Union, and Communist Party organisations in Russia, has been received by the Department of Overseas Trade from the British Commercial Mission, Moscow.

The Decree lays down the fundamental rules to be observed in connection with the construction and exploitation of wireless stations for special purposes which are stated to be industrial and commercial wireless stations, wireless stations for educational and scientific purposes, and amateur wireless stations.

The translation of the Decree may be seen by United Kingdom firms on application to the Department of Overseas Trade (Room 53), 35, Old Queen Street, London, S.W.1. (Ref. 8092/F.R./C.P.)

### ALGERIA: MINING CONCESSIONS FOR SALE.

H.M. Consul-General at Algiers has received an enquiry for the names and addresses of British firms interested in the purchase and exploitation of mines in Algeria.

The enquiry indicates the existence of a calamine deposit with exploratory workings, in addition to deposits of lead, radioactive mineral, silver and phosphate containing 60 per cent. of phosphate of lime.

A geographical and descriptive Report (in French), with analysis, can be seen by interested British firms on application to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1. (Ref. D.O.T. 11620 F.E.)

### FORMOSAN SUGAR CROP.

H.M. Consul at Tamsui has forwarded details of the first official estimate of the sugar production in Formosa for the season 1923-24, which allow for 6,031,951 piculs centrifugals and 153,578 piculs of brown sugar. The total estimate of 6,185,529 piculs would be equivalent to 365,255 tons. The area under cane is returned at 287,122 acres.

These figures, both for crop and area under cane, are below those put forward in the preliminary estimate. In the event of the present estimate being realised, the 1922-23 season's output will be exceeded by 230,731 piculs centrifugals and 47,519 piculs browns, or 278,250 piculs in all, and the forthcoming season will be second only in the results attained in the "record" year 1907, when the total production amounted to 7,634,903 piculs (450,841 tons).—(From the *Board of Trade Journal*, October 11, 1923.)

### PHOTOMICROGRAPHY.

Photomicrography as an applied science is rapidly increasing in importance, and a knowledge of its technique has often proved of great value to works' chemists.

It is perhaps not sufficiently widely known that there exists in London a young and vigorous society devoted to the study and advancement of photomicrography.

The Photomicrographic Society holds its meetings at King's College, Strand, W.C., at 7 p.m. The programme for this session includes the following:—

Nov. 14: "High Power Photomicro-

graphy," J. E. Barnard, F.Inst.P., F.R.M.S.

Dec. 12: "General Methods in Photomicrography," E. Cuzner, F.R.M.S.

Jan. 9: "The Practical Use of Filters in Photomicrography," J. H. Pledge, F.R.M.S.

Feb. 13: "The Etching and Structures of Metals and Alloys," F. A. Ruddock, A.I.C.

Mar. 12: "Low Power Photomicrography," W. H. S. Cheavin, F.C.S., F.E.S., F.R.M.S.

April 9: "Photomicrography applied to Geology," Prof. W. T. Gordon, M.A.

May 15: Annual General Meeting and Exhibition.

In addition, informal meetings for discussion and demonstrations on photomicrographic matters are held at intervals.

A medal and a certificate are awarded annually, also a sum of money is awarded for the best advance in photomicrographic technique.

Although no definite instruction in photomicrography is given by the Society, it possesses to the full the "club spirit," and its members are anxious and willing at all times to help the novice.

Visitors are welcomed at the ordinary meetings, and cards of invitation and further information about the Society will gladly be given on application to the Hon. Sec., 1, Hogarth Hill, Finchley Road, Hendon, N.W.11. E. H. ELLIS.

### MACHINE OIL FOR SOUTH AFRICA.

Mr. W. G. Wickham, His Majesty's Senior Trade Commissioner in South Africa, reports that the South African Railways and Harbours Administration are calling for tenders to be presented by the 5th November, 1923, for the supply of machine oil. (Tender No. 477).

United Kingdom firms desirous of receiving further information regarding this tender should apply to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1, quoting reference 12290/E.D.C.C./2.(B).

Mr. W. G. Wickham, H.M. Senior Trade Commissioner in South Africa, reports that the same authority are calling for tenders, to be presented by the 5th November, 1923, for the supply of antifricition grease. (Tender No. 478).

Reference, 12290/E.D./C.C./2.(C).

## LINSEED OIL FOR SOUTH AFRICA.

The Tender Board of the South African Railway Headquarter Offices at Johannesburg are calling for tenders for the supply and delivery "ex. ship" of raw and double boiled linseed oil for the six months ending 30th June, 1924. (Tender No. 476).

A copy of the specification, general conditions of tender, etc., may be seen at the Department of Overseas Trade.

## CHEMICAL INDUSTRY CLUB.

The Annual Dinner of the Chemical Industry Club will take place at the Connaught Rooms, on Friday, November 23.

Several men prominent in the chemical world will be present—names will be announced later.

Tickets, 15s. each, may be obtained from members, or from the secretary, 2, Whitehall Court, London, S.W.1.

## PROCEEDINGS AND NOTICES OF SOCIETIES.

## THE CHEMICAL SOCIETY.

ORDINARY SCIENTIFIC MEETING, THURSDAY, OCTOBER 18.

The following paper was read:—

*Studies of Electrovalency.* Part III.—*The Catalytic Activation of Molecules and the Reaction of Ethylene and Bromine*, by R. G. W. NORRISH.

## SOCIETY OF GLASS TECHNOLOGY.

The first meeting of the Society for the session 1923-24 was held at Sheffield on Wednesday, October 17.

The Vice-Chancellor of the University of Sheffield, Sir W. H. Hadow, M.A., D.Mus., made the presentation of the "Frank Wood" Medal to the successful candidates, A. R. Sheen, B.Sc.Tech., and F. Winks, B.Sc.Tech.

The following papers were received and discussed:—

*The Effect of Titania on the Properties of Glass*, by A. R. SHEEN, B.Sc.Tech., and PROF. W. E. S. TURNER, D.Sc.

*The Estimation of Selenium in Glass*, by A. COUSEN, B.Sc., A.R.C.Sc.

## ROYAL MICROSCOPICAL SOCIETY.

A Conversazione was held at the Examination Hall, 8-11, Queen Square, Bloomsbury, on Thursday evening, October 11.

There were two Lantern Demonstrations: *Some Adaptations of Marine Organisms*, by H. G. CANNON, M.A., F.Z.S., F.R.M.S.

*The Material Basis of Heredity*, by PROF. R. RUGGLES GATES, M.A., Ph.D., F.L.S., F.R.M.S.

## GENERAL EXHIBITS.

E. W. Bowell, M.A., M.R.C.S., L.R.C.P., F.R.M.S.: (a) Photomicrographs of Sections. (b) An improvement to the Automatic Microtome.

L. S. Day: Circulation in Newt.

E. H. Ellis, F.R.M.S.: Capsule of *Grimmia pulvinata*. Slides of Moss mounted in Glycerine Jelly.

George H. Gabb, F.C.S.: Eggs of the Powder Pest Beetle (*Lyctus brunneus*). (Exhibited for the first time.)

R. Ruggles Gates, M.A., Ph.D., F.L.S., F.R.M.S.: Comparison of Crossing Overstages in *Lactuca* and *Oenothera*.

F. B. Gibbard: *Arrenhurus caudatus*.

L. G. Gilpin-Brown: Legs of *Syrphid Trophidia scita*.

H. Goullee: Entomological Specimens.

J. T. Holder, F.R.M.S., and Miss Holder: Eyes of Spider.

J. R. Leeson, M.D., F.L.S., F.R.M.S.: "The Fall of the Leaf."

R. J. Ludford, Ph.D., B.Sc., F.R.M.S.: Keratin Formation (Cornification) in Cancerous Growth of Mouse.

J. A. Murray, M.D., F.R.M.S.: Iron-Alum Hæmatoxylin Preparations (27 years old).

J. C. Myles: Diatoms.

H. W. R. Room, F.R.M.S.: Marine Hydrozoa (*Obelia geniculata*), showing Development and Liberation of Sexual Gooids.

J. Smiles and F. Welch: The Elements of Dark-ground Illumination.

C. Tierney, D.Sc., F.L.S., F.R.M.S.: "The Horrors of War."

E. E. Warr: Living Diatoms.

## TRADE EXHIBITS.

R. & J. Beck, Ltd.: New form Museum Microscope. New form Dissecting Microscope, with and without Greenough Binocular. New Apertometer. Aplanatic Ring Illuminator. Focussing Dark-ground Illuminator. Aquarium Microscope. Various forms of Microscopes and Apparatus.

The British Drug Houses, Ltd.: Microscopic Dry Stains and Solutions. Mounting Media. Indicators and Buffer Solutions. Comparator Case. Microscope. Slides stained with B.D.H. Standard Stains.

Chapman & Alldridge, Ltd.: A Non-Achromatic Microscope Sub-stage Con-

denser rendered *aplanatic* by the use of a prolate spheroidal surface. A device for centring Microscope Sub-stage Condensers whose iris diaphragms are situated between their principal focus and the condenser. A combined Microscope Objective and Dark-ground Illuminator for metallurgical work. A Vertical Thin Glass Illuminator for similar work. Specimens kindly prepared by Dr. Walter Rosenhain, and lent by the National Physical Laboratory. A new Microscope Focussing and Centring Sub-stage. New "Non-Flex" Microscope Stands.

The Edison-Swan Electric Co., Ltd.: Pointolite and Fullolite Lamps.

Flatters & Garnett, Ltd.: New Series of Slides, mounted in Euparal. British-made Stains in Tablet Form.

A. Gallenkamp & Co., Ltd.: Microscopes and Apparatus.

Kawksley & Sons: Microscopes and Apparatus.

Kelvin, Bottomley & Baird, Ltd.: Microscope Illuminant. Microscope. Optical Work in Quartz.

R. W. Munro, Ltd.: The Denne Photomicrographic Camera and Microscope.

Ogilvy & Co.: Mono-Binocular Microscopes, having Interchangeable Bodies. High-power Binocular Attachment for Monocular Stands. Low-power Binocular Dissecting Magnifier, having a large field of view. Ogilvy's Electric Microscope Lamps.

Rudolph & Beesley: "Reichert" New Darkfield Condenser. "Reichert" Changeable Condenser for Transmitted and Dark-ground Illumination. New "Reichert" Opaque Illuminator. "Reichert" Stereo-Insert. "Reichert" Microscopes and Accessories.

James Swift & Son, Ltd.: Medical, Mineralogical and Metallurgical Microscopes. High-power Binocular, Micrometer Microscopes, Gonimeters, Dichroscopes, Photomicrographic Apparatus, etc.

W. Watson & Sons, Ltd.: Microscopes and Accessories. A new Immersion Dark-ground Condenser. New Condenser Mount, incorporating Centring Arrangement. A New Greenough Binocular for Petrological Purposes. A New Microscope with Interchangeable Monocular and High-power Binocular Bodies.

#### THE INSTITUTION OF ELECTRICAL ENGINEERS.

The first Ordinary Meeting will be held on October 18, at 6 p.m., when Dr. A. Rus-

sell, M.A., D.Sc., President, will deliver his inaugural address.

A good programme of Ordinary Meetings and Informal Meetings has been arranged for the coming session.

#### BOOKS RECEIVED.

*Organische Chemie*, von Dr. RUDOLF PUMMERER. Pp. XI. + 209. 1923. Verlag von Theodor Steinkopff, Residenzstr. 12b. Dresden und Leipzig.

*Molekulargrossen von Elektrolyten*, von Dr. PHIL U. CHEM. PAUL WALDEN. Pp. XI. + 350. 1923. Verlag von Theodor Steinkopff, Residenzstr. 12b, Dresden und Leipzig.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

24023—Metallbank-und Metallurgische Ges.—Sulphur furnace. Sept. 26.

24166—Williams, J. G.—Manufacture of acid phosphate salts soluble in water. Sept. 28.

#### Specifications Published this Week.

181395—Lilienfeld, Dr. L.—Manufacture of cellulose ethers.

203812—Badische Anilin & Soda Fabrik.—Process for producing formic acid derivatives.

203975—Guillemin, J.—Appliances for the reduction of scoliosis and other bone deformations.

#### Abstract Published this Week.

202157—Dyeing cellulose acetate.—British Dyestuffs Corporation, Ltd., of 70, Spring Gardens, Braddley, J., and Hill, J., of Crumshall Vale Chemical Works, Blackley, both in Manchester, and Anderson, E. B., Mill Heys, Hemyock, near Tiverton, Devon.

Acid wool and substantive dyes, dyeing with; azo dyes, forming on the material.—Cellulose acetate silk is dyed by means of aminoazo dyes containing one or more carboxylic groups but not sulphonic group, the amino group being diazotizable. The dyes may be diazotized on the fibre, and developed with the usual components. A table is given, showing the direct shades and those developed with -naphthol, -oxynaphthoic acid, and *p*-aminodiphenylamine of the dyes obtained from the following components: *m*-aminobenzoic acid and *o*-anisidine, anthranilic acid, *m*-toluidine, -naphthylamine, 4-nitro-2-anisidine, or 1:2-aminonaphthol ether; anthranilic acid and *o*-anisidine; *p*-aminobenzoic acid and aminohydroquinone dimethyl ether; *p*-aminosalicylic acid and -naphthylamine; -5-acetyl-amino-2-amino-4-methoxytoluene and -oxynaphthoic acid, the product being hydrolyzed; *m*-aminobenzoic acid, *p*-xylylene, and *m*-phenylenediamine or -naphthylamine. The fibre is dyed in an aqueous dye-bath, with or without the addition of weak acids or salts.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.



# THE CHEMICAL NEWS,

VOL CXXVII. No. 3315.

## ARE THE NATURAL GROUPINGS OF THE ELEMENTS AND THE SPECTRAL LINES OF HYDROGEN RELATED?

PART I.

By F. H. LORING.

It seems probable from Bohr's theory of the atom that there is a *place principle* involved, for the electrons automatically take up definite orbits when they are displaced outwardly, and on returning to their proper orbits definite wave lengths are revealed in the line spectrum then emitted, thus involving equally definite orbits. This is a very extraordinary phenomenon, and Bohr's formulation of the action by the use of Planck's quantum energy relation stands out as one of the great achievements of science.

It is very curious that the orbits should occur in definite places as due to definite quantised energy emissions, hence the term "place principle" stated above. There are, however, other phenomena involving a simi-

Name of Line.	Wave Length.
H $\alpha$	6563.04
H $\beta$	4861.49
H $\gamma$	4340.66
H $\delta$	4101.90
H $\epsilon$	3970.25

Referring to *The Chemical News*, 1923, CXXVII., p. 225, the five natural groups and groupings were given as 7, 9, 13, 21, 43.

The recent discovery of hafnium (= celtium, atomic number No. 72—there is a dispute as to priority of discovery of this element, so that one is facetiously inclined to think of it as "celtafium") as an element closely allied to zirconium, by Coster and Hevesy (*Nature*, Jan. 20, 1923) makes it necessary to raise the "18 level" in the wedge table originally given in *The Chemical News*, 1922, CXXV., p. 386.

It will be seen that "17" then becomes a limiting number in the wedge system, so that hafnium may bear a secondary number 4 in order to complete the series to which it belongs to the limit 17. This will be made evident by referring to the table.

lar place principle as the present writer has touched upon in his book, "The Chemical Elements," published by Messrs. Methuen, and which is due to appear shortly. Mention may be made of several relative papers by the present writer, which appeared in this Journal under the title:—"Is there an element of zero atomic number?" In particular see this Journal, 1923, CXXVII., p. 225, and the references therein should be consulted.

The foregoing studies do not, however, bring out clearly the "principle" in question, but they do lead up to it. If it is now assumed that the wave-lengths of the five main lines of hydrogen give expression to five orbital places round the nucleus of the atom, in conformity with Bohr's work, then it may only be a step to regard the periodic table as made up of natural groups and groupings, as already discussed in these pages—see citations above—and that these groups represent similar places. An attempt is here made to show an exact connection between these two "place" ideas, but before doing so a brief elementary statement of the characteristic feature of the hydrogen emission lines will be given.

Balmer, in 1885, showed that these lines could be closely formulated, which leads to the following well-known calculation:—

Formula and Calc.	Wave Length.
$3646.13 \times 3^2 / (3^2 - 2^2) =$	6563
$3646.13 \times 4^2 / (4^2 - 2^2) =$	4861
$3646.13 \times 5^2 / (5^2 - 2^2) =$	4340
$3646.13 \times 6^2 / (6^2 - 2^2) =$	4102
$3646.13 \times 7^2 / (7^2 - 2^2) =$	3970

One is therefore driven to the supposition that there should be 4 elements immediately before hafnium, bearing secondary numbers 0, 1, 2, 3. This would raise the total number of elements in the large grouping to 47; but since the last wedge is incomplete from the view of limiting numbers, a blank should follow the place occupied by uranium of atomic number 92. This would then raise the number to 48. The necessity of a lacuna of atomic number 93 was shown in a paper by the present writer in *The Chemical News*, 1922, CXXV., p. 309.

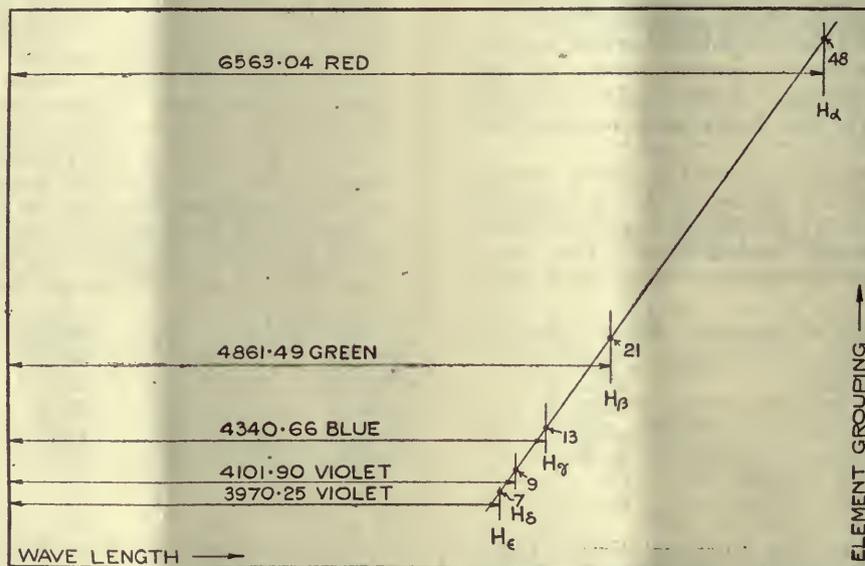
Now, plotting the numbers 7, 9, 13, 21, 43 against wave lengths of the  $\alpha$  to  $\epsilon$  lines of hydrogen, taken as the main lines, gives a straight-line curve as depicted in the accompanying diagram, which is, by the way, carefully drawn, showing that the intersec-

tions are practically perfect. The wave length values, in Angstrom units, are selected from Sommerfeld's "Atomic Structure and Spectral Lines."

It will be seen that by raising the total number of elements in the large grouping, *i.e.*, from 44 to 48, introduces 4 extra elements not determined by the atomic numbers. At the same time the limiting numbers throughout the wedge table necessitate 4 additional elements preceding hafnium. The wedge table is so complete in every possible way, in that it does not violate the chemical ideas in connection with the elements whilst giving scope for the proper expansion of the rare-earth elements from Pr to Lu, that there must be something here worth careful study. If a suggestion may

be made, it seems possible that the 4 extra elements have amalgamated with others of the series involved, for they would probably have properties already established earlier in the series; that is to say, in the first series starting with xenon.

The reader should not come to a hasty conclusion in these matters, as a very careful study of the elements at the places indicated is necessary. In counting the elements in the large grouping, it should be noted that cerium belongs to this grouping, and therefore it does not form one of the rare-earth 13. Cs, Ba, La, Hf, Ta, W, 75 and H belong also to this grouping. If the reader will refer to pages 14, 24, 28, 34, in the writer's book, "The Chemical Elements," this grouping will be made clearer.



#### NOTE ON HYDROGEN.

Inasmuch as the wedge table is made use of in this study, attention may be drawn to the group classification above given in connection with hydrogen as placed in the table. Hydrogen may be supposed to stand at the end of a very small steep wedge, so that its level will, in conformity with the other extreme levels of the respective wedges, approximate to that of fluorine, and thereby give it some characteristics that parallel well with those of the halogen elements. At the same time, hydrogen being over lithium, its electropositive character,

due to the readiness with which it parts with its single electron, is accounted for.

Now this short high wedge should contain, besides hydrogen, an element coming into the inert group, but perhaps on a slightly higher level, owing to the steepness of the wedge. Since this extra element, regarded as the *zero-atomic-number member*, was discussed in the previous papers cited (see this Journal, CXXVII., p. 225), no further argument is called for here. This note, however, shows that the wedge scheme is satisfactory, and therefore the significance of the "limiting numbers" made use of in

this study should be taken into account in probing the more obscure phase of the argument.

SUMMARY.

Plotting the values 7, 9, 13, 21, 48, at right-angles to the wave lengths of 5 main hydrogen lines gives a straight-line curve which suggests that the "place principle" of the main hydrogen orbits is fundamentally the same as the places in the periodic table as represented by natural groups and groupings containing respectively these numbers of elements in each; but a peculiarity develops at hafnium, which is discussed. It is shown that the wedge table throws some light on the problem involved in this study; and that hydrogen can be so placed, in conformity with the other elements and in no way an exception, that its two-fold property, so to speak, is accounted for. This gives the wedge table a greater usefulness and reliability in developing the argument that four extra elements may be merged or amalgamated with others so that they will have lost their separate identities.

AN EXPLANATION OF THE THEORY OF THE ROTATION OF THE ATOMIC NUCLEUS.

PART IV.

BY HERBERT HENSTOCK.

OXIDES (continued).

(Continued from Page 243.)

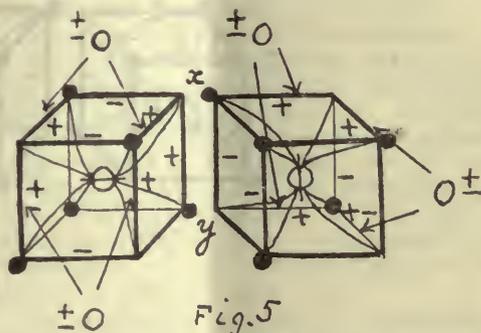
The nitrogen octet is distorted, thus exhibiting no free valencies, but it may be easily opened up in the direction of the dotted lines, when bonds would be formed permitting other atoms to join the molecule, which explains the ease with which this compound unites with oxygen.

It is often stated that nitric oxide is the most stable of the oxides of nitrogen, and with respect to the effects of heat this may be the case; but in its behaviour to the action of other atoms it is the weakest of the nitrogen oxides, as witness its spontaneous union with oxygen.

The halogens will unite with the positive edge (a-d), see Fig. 4, compounds of this nature being unstable (rule 2): oxygen will unite with the face a-b-c-d to form a double bond in NO<sub>2</sub>, but there will then be two electrons at (c), which makes the bond a

weak one (rule 6), with the consequence that the oxygen is easily detached.

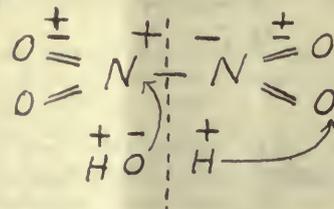
Nitrogen tetroxide, in Fig. 5, the cubes representing nitrogen atoms.



The oxygen is united by double bonds as represented in Fig. 4.

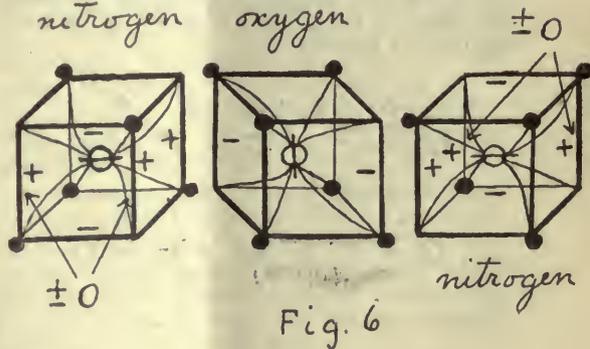
There will be two electrons at x and two at y (Fig. 5), the single bond will therefore be weak (rule 6).

When this gas is dissolved in water, a mixture of nitrous and nitric acids is formed. If the explanation of this be written with the correct polarity signs included, the mechanism of the reaction becomes plain.



The OH unites with positive nitrogen and the hydrogen with one of the negative bonds of oxygen, the double bond between this and the other nitrogen becoming a single bond, a negative edge of the oxygen linking with a positive edge of the nitrogen.

Nitrogen tri oxide in Fig. 6.



Nitrogen pentoxide in Fig. 7.

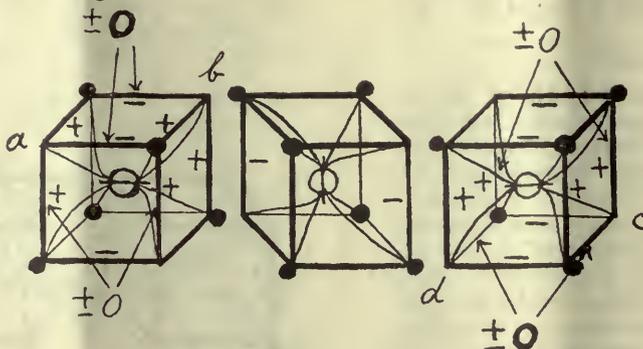
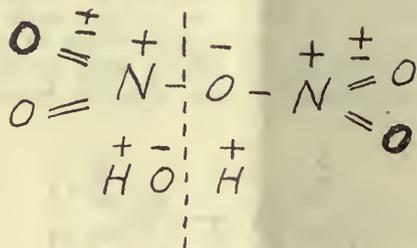


Fig. 7

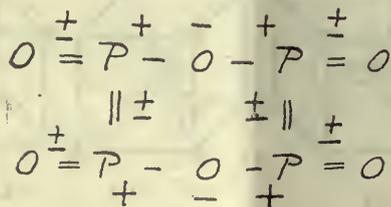
It will be seen that at *a* and *b* there will be two electrons, and the same thing applies to *c* and *d*, therefore the bonds uniting these two nitrogen atoms to the middle oxygen will be weak enough to be broken by water; thus:



Those bonds uniting the two oxygen atoms (marked dark) to the nitrogen will be weak, from the same cause, and these oxygen atoms are therefore the *nitrite* oxygen, which splits off to form nitrite.

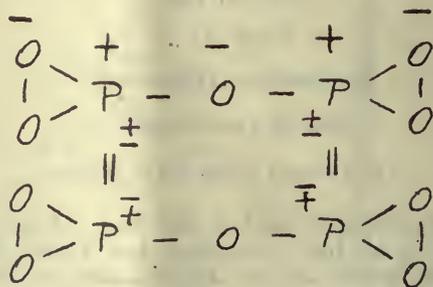


Phosphorus tri oxide is usually written  $\text{P}_2\text{O}_3$ , but the vapour density agrees with the formula  $\text{P}_4\text{O}_6$ , it will probably be constituted as follows:—



That is, it will be like  $\text{N}_2\text{O}_3$  given above, but the molecule is doubled, a spare double bond being free in each nitrogen atom of  $\text{N}_2\text{O}_3$ , and this would apply equally to  $\text{P}_2\text{O}_3$ .

Phosphorus pentoxide, if it exists as such, will be like  $\text{N}_2\text{O}_5$ , see Fig. 7, but the double molecule,  $\text{P}_4\text{O}_{10}$ , will be probably



which can be easily seen on drawing out the octets.

The oxides of arsenic, antimony and bismuth will be constituted similarly to the oxides of nitrogen.

Chemical Research Laboratory,  
School Gardens,  
Shrewsbury.

SOME RECENT RESEARCHES IN  
ORGANIC CHEMISTRY.

By R. F. HUNTER, F.C.S.

*(Continued from Page 245.)*

Skri Krishna, and Pope, the first of these, condensation of *m* dimethylamino phenol with benzaldehyde included the preparations of 4 dimethylamino 2 hydroxy benzhydrol and a number of derivatives.

The second paper dealt with phenol citraconin, and included the preparation of K salt, tetra bromo derivative, and the diacyl and dizenzoyl derivatives.

Another paper appearing about this time was one by Fargher and King on the additive compounds of antihyrylamino diacetic acid, the experimental part of which included the study of the salts of antihyrylamino diacetic acid, the additive compounds of anti-hyrylamino diacetic acid with neutral salts, the additive compounds of the salts of anti-hyrylamino diacetic acid with neutral salts, and the preparation of the ethyl ester of anti-hyrylamino diacetic acid.

Meanwhile the quantitative reduction by hydriodic acid of halogenated malonyl derivatives was being studied by Whiteley and West, the first part which concerned itself with the amides and S Di-alkyl and aryl substituted amides of Mono and Di bromo malonic acid, appeared about this time. The experimental work was of considerable magnitude. Bromomalonic acid,  $\text{CH Br (CONH Me)}_2$ , was prepared from malonamide, bromomalonic dimethylamide,  $\text{CH Br (CONH Me)}_2$ , was prepared from Malondimethylamide, bromo malondiethylamide,  $\text{CH Br (CONH Et)}_2$ , and the dibromo compound,  $\text{C Br}_2 \text{ (CONH Et)}_2$ , were obtained from Malondiethylamide. The corresponding compounds from malondi n propylamide,  $\text{CH Br (CONH Pr)}_2$ , and  $\text{C Br}_2 \text{ (CONH Pr)}_2$ , the bromo compound,  $\text{CH Br (CONH C}_4\text{H}_9)_2$ , from malondi n butylamide, the iso compound from malondi isobutylamide, the compounds,  $\text{CH Br (CONH CH}_2\text{Ph)}_2$  and  $\text{C Br}_2 \text{ (CONH CH}_2\text{Ph)}_2$ , from malondibenzylamide, bromomalonyl diurethane,  $\text{CH Br (CONH CO}_2\text{Et)}_2$ , from malonyldiurethane. A number of other bromo compounds were also prepared.

The reduction of ureides of mono and dibromo malonic acids by HI, and of bromo ketones by HI, were also studied.

From the same college (the Royal College of Science) appeared Naik's paper on the formation and properties of dithio ke-

tones ( $\text{R}_2\text{C : S : S}$ ) and di thio ethers ( $\text{R}_2\text{S : S}$ ), which included the preparation of di thio mesonanilide,  $(\text{NH C}_6\text{H}_5\text{CO})_2\text{C : S : S}$ , its nitration, bromination, hydrolysis and reduction.

Other disulphide bodies were isolated.

About the same time, Pope and Smith's paper of  $\text{S}_2\text{Cl}_2$ , on substituted ethylenes, in which  $\beta\beta'$  Dichlorodipropyl sulphide,  $(\text{C H Me Cl CH}_2)_2\text{S}$  and  $\beta\beta'$  dichloro-di-sec-butyl sulphide  $(\text{C H Me Cl CH Me})_2\text{S}$ , were described, another paper on  $\beta\beta'$  dichlorodiethyl disulphide appeared by Bennet, in which the following were investigated:

Oxidation of  $\beta\beta'$  dichlorodiethyl sulphoxide to a sulphonic acid.

The preparation of monothio ethylene glycol,  $\text{SH CH}_2\text{CH}_2\text{OH}$ , of  $\beta\beta'$  dichlorodiethyl disulphide and the oxidation of the disulphide.

Some experiments on the production of compounds containing arsenic as a centre of optical activity were described by Barrow and Turner, which necessitated the study of

$\gamma$  Phenyl propyldimethylarsine;  
Phenyl  $\gamma$  phenylpropylmethylarsine;  
As - Methyl tetra hydro arsinoline;  
Phenyl  $\alpha$  naphthylmethylarsine and its oxide.

Hydroxy phenyl  $\alpha$  naphthylmethyl arsonium d  $\alpha$  bromo camphor II sulphonate;

Methyl ethylio do arsine;  
Phenyl  $\alpha$  naphthyl methyl allyl arsonium bromide;

Phenyl and naphthyl benzylmethyl arsonium bromide.

Three papers now appeared together: One on the action of alkyl nitrates on piperidine, by Gibson and Macbeth, in which the action of ethyl, propyl and butyl nitrate on piperidine was studied. The second was on Friedel Crafts Reaction, Migration of halogen atoms in the benzene nucleus, by Coisarow. The third was by Green and Price on the Chlorovinyl chloroarsines. Among the compounds investigated in this research were  $\beta$  Chlorovinyl dichloroarsine,  $\text{CH Cl : CH As Cl}_2$ ,  $\beta\beta'$  Dichlorovinyl chloroarsine  $(\text{CH Cl : CH})_2\text{As Cl}$ , and  $\beta\beta'\beta''$  Trichlorotrivinylarsine  $(\text{CH Cl : CH})_3\text{As}$ .

In February, 1921, Kenner and Stubbings communicated to the Chemical Society's *Journal* a paper on the second form of 6 : 6' Dinitro diphenic acid and its conversion into new cyclic systems, in the experimental part of which were the preparations of 2-Chloro-3-nitrobenzoic acid.

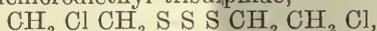
$\gamma$  6 : 6'-Dinitro-diphonic acid;  
 6 : 6'-Diamino-2 : 2'-ditolyl;  
 $\gamma$  6 : 6'-diacetylaminodiphonic acid;  
 the di lactamo of  $\gamma$  6 : 6'-diaminodiphenic  
 acid and 1 : 10-dimethyl-5 : 6-naphtha iso-  
 diazine.

The following month Morgan and Grist investigated their aryl sulphonyl naphthylene diamines and sulphonic acids, describing a variety of new compounds.

Meanwhile, a further research on residual affinity and co-ordination, reaction of selenium and tellurium acetyl acetones, appeared by Morgan and Drew, in the experimental part of which we have

Tellurium-O-ethylacetylacetone trichloride,  $\text{CH}_3\text{C}(\text{O C}_2\text{H}_5):\text{C H C O CH}_2\text{Te Cl}_3$ , and its derivatives, and the reactions of selenium acetyl acetone.

This was followed by another paper on the action of  $\text{S}_2\text{Cl}_2$  on ethylene, in which we get dichlorodiethyl trisulphide,

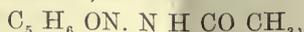


Pseudo solutions of S in  $\beta\beta'$ -dichlorethyl sulphide, and the study of the absorption of  $\text{C}_2\text{H}_4$  by  $\text{S}_2\text{Cl}_2$ .

In March, 1921, Scott and Cohen's work on the carbamido acids and their hydrantions appeared, in which the preparation of o-Acetyl-carbamidobenzoic acid,  $\text{N H Ac C O N H C}_6\text{H}_4\text{CO}_2\text{H}$ , and the corresponding o-Benzoyl carbamidobenzoic acid are described, and a fairly complete study of carbamidophthalic acid and its hydrantion is given. The action of sodium hypochlorite, methyl sulphate, etc., on hydrantoin are described.

Papers have appeared on the Organic Derivatives of Thallium, by Goddard, in which thallium dimethyl carbonate, chromate, nitrate, thiocyanate, thallium, diethyl chromate and thallium diethyl trichloro acetate are described, and on organic derivatives of tellurium, the action of ammonia and alkalis on and dimethyl telluronium di iodide, by the late Richard Henry Vernon.

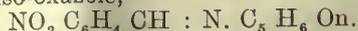
One of the series of papers on non-aromatic diazonium salts, 3 : 5-Dimethyl-iso-oxazole-4-diazonium salts and derivatives, by Morgan and Burgess, appeared at this time. Among the preparations we have 4-nitro-3 : 5-dimethyl iso oxazole 4-amino-3 : 5-dimethyl-iso-oxazole and its hydrochloride; 4-acetyl-amino-3 : 5-dimethyl-iso-oxazole,



4-Benzylideneamino-3 : 5-dimethyl-iso-oxazole,



4-o-Nitro-benzylideneamino-3 : 5-dimethyl-iso-oxazole,



3 : 5-Dimethyl-iso-oxazole-4-azoresorcinol, and 3 : 5-dimethyl-iso-oxazole-4-azo- $\beta$ -naphthylamine.

A paper by Fargher and Pyman on 4- $\beta$ -methyl amino ethylglyoxaline appeared in May, 1921. The work was important, since 4- $\beta$  aminocethyl glyoxaline is isolated from ergot, and is an intense stimulant of plain muscle. Among the experimental preparations were:

$\alpha$ -Chloro- $\beta$ -glyoxaline 4-propionic acid d-1- $\alpha$ -methyl amino  $\beta$ -glyoxaline-4-propionic acid, 4- $\beta$ -methyl-amino ethyl glyoxaline dipierate and dihydrobromide.

Cohen's paper on hydrogenated quinolines is also worthy of mention, and describes the preparation and properties of a number of interesting substances.

May, 1921, saw another paper on studies in the camphane series, amino phenylamino camphor, by Forster and Saville.

In the experimental work we have the nitration of phenylamino camphor and the nitrosoderivative, p-amino-phenyl-amino-camphor, derivatives of p-benzeneazophenyl amino camphor-p-sulphobenzeneazophenyl-amino camphor and 4-amino-1-naphthyl-amino camphor.

Two papers have appeared by Kipping and Sands on the organic derivatives of silicon, the first of which dealt with saturated and unsaturated silico hydrocarbono,  $\text{Si}_4\text{Ph}_8$ . They investigated the action of sodium on diphenylsilicon dichloride, and that of iodine on unsaturated silico hydrocarbon, giving octa phenyl di iododisilicotetrane,  $\text{Si}_4\text{Ph}_8\text{I}_2$ .

The actions of tetra chloroethane and of boiling  $\text{C}_6\text{H}_5\text{NO}_2$  on the unsaturated silico hydrocarbon were also investigated.

Their second paper was on the use of piperidine as an analytical reagent.

At the same time there appeared Davies' two papers on the cumulative effect of chlorine atom and methyl and sulphonyl chloride groups on substitution in benzene nucleus. This necessitated some important preparations.

Davies summarised his results in something of this way:

The nitration of 2 chloro p toluene-sulphonyl chloride leads to 2-chloro-5-nitro-p-toluenesulphonyl chloride and 2-chloro-6-nitro-p-toluenesulphonyl chlorides. The proportion of these isomerides shows orientation due to chlorine atom is much greater

than united directive effects of methyl and sulphonyl groups. The sulphonyl group and not the nitro is reactive in the 5-nitro, and can be replaced by OH by boiling with dilute NaOH.

Monochlorination at 70° of chloro-p-toluene sulphonyl chloride leads mainly to 2 : 6-dichloro-p-toluene sulphonyl chloride.

The second paper contained the preparation of 6-chloro-o-toluene sulphonyl chloride, 6 chlorosaccharin, the nitration of 6-chloro-o-toluenesulphonyl chloride 6-chloro-3-nitro-o-toluenesulphonyl chloride gave 6-chloro-4-nitro-o-toluenesulphonyl chloride.

Monochlorination of o-toluenesulphonyl chloride in presence of  $SbCl_5$  leads to formation of isomerides 6-chloro-o-toluenesulphonyl chloride in 40 per cent. yield nitration at 25° of this results in production of 6-chloro-4-nitro-o-toluenesulphonyl chloride and the 3-nitro compound and the sulphonyl chloride is replaced by OH by boiling with NaOH solution.

Field's paper on mitragynine and mitraversine, two new alkaloids from species of mitragine is worthy of note. Published in conjunction with it was Stedman's New Degradation product of Physostigmine. At the same time, June, 1921, there appeared Brady and Bowman's research on Dinitro tolyl hydrazines, published at this time, and included the study of several nitro-toluene and hydrazine derivatives.

The first of Barnett's studies in the anthracene series appeared at this time, and included some unusual preparations such as 9 : 10-dihydro anthraquinylidipyridinium dibromide, on which the action of NaOH,  $NH_3$ , primary and secondary aliphatic amines, pyridine and quinoline, and primary and secondary aromatic amines was studied.

Published at the same time was a paper by Challenger and Allpress on organic derivatives of bismuth. Among some of the compounds prepared by these researchers were :

Di a naphthyl chlorobismuthine, the corresponding bromo compounds and naphthyl bismuthine dibromide, phenyldibromobismuthine, and tri m tolyl bismuthine and the action of Grignard reagents on various of these and other compounds was also investigated.

## THE EVOLUTION OF CHEMICAL TERMINOLOGY.\*

BY JAMES F. COUCH.

(Continued from Page 253.)

The most inclusive definition of the term hydroxide is the statement that it denotes a substance which contains an hydroxyl group.

Defined in this way the class hydroxide will contain a very diverse collection of substances. In addition to the metallic hydroxides we shall include the oxy-acids, such as sulphuric acid and phosphoric acid and, of course, we must admit the acid salts, such as sodium bisulphate  $NaO.SO_2.OH$ , as well as the basic salts. Alcohols, phenols, the enol forms of tautomeric ketones must also be admitted. Resorein, then, may be termed orthosalicyl hydroxide. All of the organic acids, both the carboxylic and sulphonic acids, belong in this class; we shall term formic and oxalic acids hydroxides. The hydroxy-acids, such as lactic acid, have a double claim to recognition as hydroxides owing to their content of two hydroxyl groups. The hydroxy-amines, hydroxy-pyridines, hydroxy-quinolines, and the derived alkaloids amidst the intricacies of whose constitutional formulas nestles an hydroxyl group, all come clamouring for inclusion. Nor can we bar out that great class of hydroxyl compounds, the carbohydrates from glycollic aldehyde, the simple biose, through the whole class to the complex cellulose, for the carbohydrates bristle with hydroxyl groups.

There are certain difficulties, however, which arise as a result of so wide an extension of the meaning of the term hydroxide. If all these substances are to be considered hydroxides, it follows that they must have names in conformance with this aspect of their constitutions. Systematic classification requires this. But an effort to satisfy that demand would lead us into absurdity and cause us to coin a large number of new names which would be of no other service than to bolster the theory. Sulphuric acid must become sulphuryl hydroxide; sulphurous acid, thionyl hydroxide; and what we should name thiosulphuric acid and tetrathionic acid is not very clear. Phosphoric

\* [Reprinted from "The American Journal of Pharmacy, Philadelphia, Pa., July, 1923.]

acid would easily become phosphoryl hydroxide; but what should we name hypophosphoric acid? With the alcohols and phenols there would be no more than moderate difficulty; the organic acids, however, would not be so readily disposed of, and the carbohydrates would present a problem which is not at all pleasant to contemplate.

A more serious objection to the broad definition arises from the consequences to chemical theory. If we apply the term hydroxide to such a varying and heterogeneous array of substances, the concept hydroxide loses all specificity as a functional mark; it converts the term into a mere character and divests it of all practical value. The far larger portion of the substances enumerated is not chiefly characterised by the content of hydroxyl but the chemical properties depend upon other atomic complexes and the presence or absence of hydroxyl is frequently of very minor importance. The class loses most of its significance and its members no longer possess outstanding common properties.

The extension of the class to include all hydroxyl compounds serves no scientific or practical purpose. If the class cannot be considered a homogeneous unit, and it certainly cannot be so considered if it is to contain acids, bases, and alcohols, which have their own specific properties as classes, the utility of the term for either purpose is much impaired. If the members of the class do not exhibit certain properties which readily identify them as belonging to the category, and all of these various classes enumerated above do not fulfil this requirement, it is impossible to assign definite characters to the class, and consequently the significance of the class-term is destroyed.

From such considerations we must conclude that the extension of the term hydroxide to include all hydroxyl-compounds could have but one consequence, the worthlessness of the term. The second idea, that of allowing the term to embrace all hydroxyl compounds but of restricting its use to basic compounds, does not avoid the objections raised against the other inclusive idea and creates its own objection on the ground of vagueness.

There remains, then, the concept that an hydroxide is an hydroxyl-compound with basic properties. This most limited definition excludes the oxy-acids, the alcohols, the phenols, enol-ketones, organic acids, sulphonic acids, and all the rest of that galaxy admitted by the broad definition.

The first point in favour of this narrow view is the fact that this concept is the one which is held by the greater number of chemists at the present time. This, in itself, is no argument for the correctness of the concept, but it is an important consideration in a case like the present, where the preferableness of conflicting notions is being studied. It would be easier to get general agreement to this definition than to any other.

Although this narrow definition is supported by the historical data, an argument based upon whose facts will not be considered of first importance. We cannot consent to bind ourselves to the notions of a hundred and twenty years ago, for we know that those ideas of chemical relationships were inaccurate in the light of our present knowledge. We can, by such evidence, readily demonstrate that the term acid is misused to-day, and, indeed, that term has had many modifications of meaning since Lavoisier's time; but such an effort could not result in any real benefit to chemical nomenclature. Certainly, no general term is to-day used with more specificity of meaning than is the word acid. Consequently the historical facts, while important, cannot be considered final reasons for the acceptance of this narrow view.

A more important argument in support of this limited concept, however, is based upon functional relationships. Throughout chemical nomenclature the idea of functional similarities is most important in classification. The acid function is the only property shared in common by all the members of the large, perhaps the largest, chemical classification of substances, the acids. Diverse as their structure may be, various as their components are, differing most widely in physical properties, in solubility, in state of aggregation, yet all producing hydrogen ions under proper circumstances, whence hydrogen ion concentration comes to be the measure of acidity. The possession of this one function classifies the substance as an acid.

Is there a corresponding function which characterises an hydroxide? Unless we limit the term to the basic hydroxides, those which, when soluble, ionise to radical and hydroxyl ions in solution, it will be difficult to find one single common property among hydroxyl compounds. Reactions with phosphorus halides, which are of broadest application, will not suffice definitely to distinguish them in every case.

It appears likely that the confusion



which has arisen out of the idea that oxyacids are hydroxides is due to lack of just this sort of consideration. This concept apparently had its beginnings at the time when chemical theory decided that water is necessary for the acid function and the natural analogy of both acidic and basic oxides combining with water to form in the one case acids and in the other bases was too alluring for resistance. This conclusion was brought forward a few years before Arrhenius published its revolutionising theory; it is quite probable that, had the theory of ionisation been accepted first, no acid would ever have been termed an hydroxide. Happening in the other way, however, and in the face of the numerous new ideas consequent upon the electrolytic hypothesis, the study of water combination was neglected, and such imperfect ideas as had been formulated were allowed to stand unchallenged.

From no functional point of view, then, can an oxy-acid be considered to fall into the class of hydroxides. On the contrary, the very opposite properties of acids and basic hydroxides indicates fundamental differences in the nature of the combined hydroxyl groups. In the one case the hydroxyl group is split by ionisation, its hydrogen appears as hydron, and its oxygen occurs in the anionic portion of the electrolyte. In the basic hydroxides the hydroxyl ionises as such.

Another fundamental distinction will become apparent if the mechanism of the reaction between ionised water and an acidic oxide is compared with that of ionised water with a basic oxide.

The same argument applies when we consider the alcohols as hydroxides. These, when they ionise, yield hydrogen ions only, never hydroxyl ions. For theoretical reasons they are sometimes considered as basic hydroxides, yet this concept cannot justify itself in the face of critical analysis. Many of the ideas we hold concerning the alcohols are the result of the pedagogical practice of comparing them with the alkaline hydroxides for the sake of impressing the facts of organic chemistry upon our student minds. True, we have a series of "salts" of the alkyl radicals and can match the more important mineral salts with examples from the organic compounds. But it is not difficult to see that there is a fundamental difference between the two classes of substances. Methyl chloride, to consider a well-known alkyl "salt," is no

chloride in the sense that sodium chloride is; it does not ionise to form chloride ions until it has first been hydrolysed. It is rather chloromethane, and this is the preferred terminology; the other name is retained for historical and commercial reasons.

In the phenols the hydroxyl group also lacks any basic function, and here, when there is any ionisation, hydron and not hydroxyl ion is formed. The replacement of the phenolic hydroxyl by anions does not result in true salts. This is recognised in their nomenclature; we speak now of chlorobenzene, not of phenyl chloride, and of chlorophenol, not of salicyl chloride (which indeed would be a quite different substance).

In the hydroxy organic acids the hydroxyl has no basic functions whatever, and the consideration of these compounds as hydroxides would lead to such a cumbersome nomenclature that the Geneva system is much to be preferred. Yet these substances must be included in the class hydroxide unless we are to define it narrowly.

In the nitrogen organic compounds the presence of hydroxyl is always of minor importance. Where the hydroxyl is united with the ring nitrogen we have the pyridinium, quinolinium, etc., bases, which are true basic hydroxides, analogous with ammonium hydroxide. Hydroxyl, substituted in the ring, however, becomes phenolic and is no longer basic. The same situation occurs with those alkaloids which add water to the basic nitrogen atom to form true hydroxides; the hydroxyl so combined functions as an anionic group. When the hydroxyl is combined with carbon in the alkaloidal molecule it functions as a phenolic or as an alcoholic group.

The phenomenon of amphoteric hydroxides appears, at first glance, to present difficulties in the way of limiting the term hydroxide to basic compounds. The hydroxides of aluminium, zinc, chromium, lead, etc., dissolve in acids and in strong alkalies to form, in the one event, salts of the metal, and in the other, compounds which have been considered metallic aluminates, zincates, chromites, plumbates, and so on. Creighton\* has just reported the formation of metallic salts of cupric acid by the solution of cupric hydroxide in strong alkalies. As representative of this class of phenomena, with the possible exception of

\* *J. Am. Chem. Soc.*, 45, 1237 (1923).

the last case, let us consider the case of aluminium hydroxide.

From the evidence it might be argued that aluminium hydroxide may behave either as an acid or as a base and, indeed, the term "amphoteric" was coined to describe just this condition. If there is any validity in such an argument we must postulate the dissociation of aluminium hydroxide in solution, however slight the concentration may be, into not only hydrogen and hydroxide ions, but into aluminium and aluminate ions. The mere statement of the logical consequences of the idea at once demonstrates that it is preposterous. No one will to-day question the conditions which follow the solution of aluminium hydroxide in strong acid. There is agreement that this process is analogous to the solution of any metallic hydroxide in a strong acid. This settles the question of the basic behaviour of aluminium hydroxide. What, then, shall we say about the solution of this substance in strong alkalies? If it develops an acid function we must postulate dissociation of hydrogen; if we wish to escape from this absurdity we are forced to deny the actual formation of sodium aluminate.

This is not, of course, the *impasse* that it appears to be. The way out of the difficulty lies in a criticism of our use of the word solution in this connection, and when we carefully consider this point we see at once that we cannot view the acid and alkaline "solutions" of aluminium hydroxide as qualitatively similar. There need be no question of hydrogen ion formation here at all, for we are really dealing with a two-phase system in which micels of aluminium hydroxide surrounded with an envelope of adsorbed sodium ions form the dispersed phase. In other words, the system belongs to colloid chemistry, and considerations of the formation of a sodium salt are quite beside the point. Aluminium hydroxide is a base, a weak base, to be sure, but a base, nevertheless, and it is peptised by sodium hydroxide.

The same reasoning may be applied to the "amphoteric" hydroxides of zinc, chromium and lead, which are dispersed in alkaline solutions and which the older chemistry considered might form compounds known as zincates, chromites, and plumbates. The case of cupric acid cannot, according to Creighton, be disposed of in this way, yet he makes no assumption of the dissociation of cupric hydroxide to form hydrogen ions, assuming, rather, that the cuprate ion re-

ceives its two negative charges from negative hydroxyl ions. This view cannot, of course, affect the truly basic character of cupric hydroxide.

But if we are to limit the term hydroxide to basic compounds, what term shall we use to designate the larger class included in the broader definition of the word? If we must have some way of designating all substances which contain hydroxyl groups, they may conveniently be referred to as hydroxyl compounds. This, indeed, describes them much better than the term hydroxide, for the first phrase refers definitely to a structural similarity just as the phrases carbon-compounds, nitrogen-compounds, or sulpho-compounds, do, and without binding us to any specific statement as to functional characteristics.

On the contrary, it may be urged that the term bases is sufficient for the basic hydroxides, and with some show of reason. The term base may, however, include substances which do not contain hydroxyl groups and which do not react with water to form them. Witness the "onium" bases, many of which do not form OH.

From all these considerations it appears that the greatest practical as well as scientific utility will be served by the limited concept of the term hydroxide.

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#### GENERAL NOTES.

##### GERMANY'S TRADE AND INDUSTRY IN SEPTEMBER.

The Commercial Secretary at Berlin (Mr. J. W. F. Thelwall) has forwarded to the Department of Overseas Trade a review of Germany's trade and industry during September.

The devastating effect of the occupation and separation of the Rhineland and the Ruhr district may now be seen in all branches of German industry. The heavy fall of the mark as a result mainly thereof caused a great increase in the prices of all materials and in wages; and as, owing to the too substantial and rapid currency depreciation, it was impossible for industry to obtain the requisite capital, the existing shortage of capital and credit in trade and industry was greatly accentuated in the month under review, particularly as the Reichsbank were compelled by circumstances to restrict the granting of credit still further. Partly for these reasons, and also owing to the heavy burden of taxation, the world's market prices were reached or exceeded in more and more spheres of trade and industry. The consequences were increased stagnation in sales and further restrictions of work.

The reports of the Chambers of Commerce show that, although further large portions of trade and industry have gone over to the system of calculating prices in gold marks, no final solution of the difficulties presented by the currency depreciation has been arrived at so long as a stable cur-

rency depreciation has been arrived at so long as a stable currency has not been created, enabling all branches of industry, including the retail trade, to fix prices on a stable basis and to ensure the counter-value for deliveries and services.

##### Mining.

In the Central German brown coal district the output increased as compared with the preceding month, which was affected by strikes. The demand for raw coal declined towards the end of the month. The production of wet press bricks came to a standstill in September. The call for briquettes was greatly restricted, so that it was necessary, in part, to produce for stock. Coal prices rose in the period from the 1st to the 10th of September in proportion to the advance in wages and salaries and, in virtue of the negotiations in the Reich Coal Council, were fixed on a gold mark basis as from September 17. In fixing wages, arbitration was twice resorted to.

In Upper Silesia the pit coal production fell off, as there were two less working days in September as compared with the preceding month. Strike movements in various pits also interfered with production. As in the other coal districts, the calculation of coal prices in gold marks was introduced in Upper Silesia as from September 17. Calculation in gold marks was urgently necessary, as the heavy losses resulting from the former paper mark prices, owing to the rapid currency depreciation, could no longer be borne by the pits. In consequence of an anticipated substantial rise in prices, the demand for coal increased at times, but, in general, it was exceedingly weak, mainly in view of the lack of working capital in industry and of the want of purchasing power on the part of household coal consumers.

##### Potash.

In the potash industry there were fewer sales than in the previous month. Shifts had, in consequence, to be dropped, and the dismissal of workers could no longer be avoided. Potash prices were repeatedly increased, but in no way kept pace with the advance in prices of all materials, fuel, and explosives, and with the rise in wages and salaries. Agriculture held back with orders on account of lack of money. Only sulphate of potash products could be sold to a certain extent to foreign countries, frequently, however, only at a loss in consideration of the position of the world's market prices. A large part of the production had to be taken into stock.

#### *Petroleum.*

In the petroleum industry the profits of the works declined in consequence of the increase in wages and costs. The degree of employment continued, however, satisfactory. Owing to long-dated contracts for delivery, sales are ensured for some time ahead.

#### *Metal Industry.*

The metal market was adversely affected by the general situation. German metal prices have, in part, risen above the world's market level. This applies specially to lead. The metal industry continued to limit its purchases and only to cover absolutely essential requirements, with the result that a minimum amount of business was transacted in the month under review.

#### *Aluminium Industry.*

In the aluminium industry in Lüdenschaid and neighbourhood, employment was poor. Inland and foreign sales were bad, as the purchasing power of the inland population has declined still further, and increasing foreign competition renders export more and more difficult. The Customs policy of foreign countries also hampered export. The same applies to other products of the Lüdenschaid finished metal goods industry.

#### *Electrical Industry.*

The position of the electrical industry became worse, particularly as the cutting off of the occupied territory has greatly restricted the market for its products. Customers could, in part, no longer raise the requisite capital for new orders. Practically no extensions of industrial plant and overland power stations are being carried out. Prices have exceeded those of the world's market.

#### *Chemical Industry.*

Foreign sales of chemical preparations have declined to an alarming extent. The existing stock of orders is considerably below that which is normally on hand, both as regards quantity and value. In the interests of the workers, restrictions of operations have, so far, not been introduced, though this will be difficult to avoid in the event of the continuance of present conditions.

#### *Glass Industry.*

Employment in the sheet and hollow glass industry fell off. The shortage of working capital and the exceptionally high rate of interest for bank credits rendered production very much more difficult. The industry was forced to go over to calculation in gold marks. Inland and foreign sales, in

consequence, were quite unimportant. Prices obtainable abroad were so low that the works were, in part, not even able to secure half the absolutely necessary inland price.

#### *Paper Industry.*

The position of the Berlin envelope industry became worse. Still fewer orders were received, and the number of workers, who had latterly been working only three days a week, had, therefore, to be again cut down. The shortage of money would not permit of any new purchases of raw materials. The available stocks, so long as they lasted, were, therefore, worked up. Wages rose very considerably. In consequence, it appeared doubtful whether it would be possible to continue work for even two or three weeks longer.

The entire German printing industry found itself in a serious position. All firms in the type-founding industry had been working short time since September 1, the majority only 24 hours. The position of the newspaper printing works was the most difficult. That of the jobbing and book printers was similar; it was only with the greatest effort that they were able to raise sufficient money for the payment of wages, salaries, and for the purchase of printing paper. Orders from abroad came in sparingly, as the chief markets, Switzerland, Holland and Scandinavia, owing to the general dullness of business prevailing there also, were no longer very capable of purchasing. There is no prospect of an improvement in the situation. It is more likely that further considerable restrictions of work will have to be reckoned with in the immediate future, as, in view of the difficult economic conditions generally, firms are not in a position to work for stock. Zinco-graphic works also have been working half-time for weeks; besides the curtailment of hours, dismissals have also had to be resorted to.

#### *Leather Industry.*

The prices for raw hides and skins advanced 40-50 fold, as compared with the preceding month, in proportion to the currency depreciation. As a result of the difficult financial conditions, only the most necessary requirements were covered. There was a brisker demand solely for ox and cow hides and calf skins. On the leather market business was stagnant practically the whole of the month. The position on the boot and shoe market was still worse, as, owing to the rapidly increasing prices, buyers were almost completely absent.

### DISINFECTANT FLUID FOR SOUTH AFRICA.

Mr. W. G. Wickham, H.M. Senior Trade Commissioner in South Africa, reports that the South African Railway Administration are calling for tenders for the supply of disinfectant fluid during the period January 1, 1924, to June 30, 1924. (Tender No. 482.)

A copy of the tender form, specification, and conditions of tender is available for inspection by United Kingdom firms at the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1. (Ref. No. 12337 E.D./C.C. (2).)

The South African Railway and Harbours are calling for tenders, to be presented by November 12, 1923, for the supply of red oxide paint in paste, during the period January 1 to June 30, 1924. (Tender No. 481.)

A complete set of documents comprising general conditions of stores contracts, tender form and specification may be inspected at the Dept. of Overseas Trade.

### CHEMICALS (COAGULANTS) FOR SOUTH AFRICA.

The Rand Water Board are calling for tenders (contract No. 249) for the supply and delivery of 150 short tons, or alternatively 300 short tons, aluminium sulphate or alumino-ferric, on or before noon on Friday, November 9, 1923. Reference No. 12342/E.D./C.C./2.

### BRITISH EMPIRE CANCER CAMPAIGN.

#### PROGRESS OF THE APPEAL.

By consent of the Ministry of Health and the Stationery Office, the organisers of the British Empire Cancer Campaign have acquired the right to publish the recently issued report of the Ministry of Health Committee on Cancer. This will shortly be available, and to be obtained free on application to the Secretary, British Empire Cancer Campaign, 19, Berkeley Street, W.1. Other literature in the form of leaflets, pamphlets, etc., is also available for distribution, and applications from all who desire information on the objects of the campaign will be readily complied with.

Preparations are well advanced for an intensive campaign throughout the country, which will be conducted through the local branches of the Red Cross, and will culminate in a "Cancer Week" to be held early in 1924.

An interesting feature of recent collec-

tions has been the ready response to appeals made from the stage by popular music hall artistes. The Holborn branch of the Red Cross has organised collections at the Holborn Empire and other music halls of the Gulliver circuit. Miss Marie Kendall, Miss Lucille Benstead, and other well-known performers have addressed their audiences during the interval, and altogether about £1,000 has been collected by these means in the past few weeks.

Subscriptions to the Campaign Fund continue to be received in a steady stream at the offices of the British Red Cross Society. A very much larger sum, however, is required if the aims of the Campaign are to be carried out speedily. Subscriptions should be sent to the Hon. Arthur Stanley, G.B.E., C.B., M.V.O., British Red Cross Society, 19, Berkeley Street, W.1, or to any of the branches of Lloyd's Bank.

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### ROYAL MICROSCOPICAL SOCIETY.

20, HANOVER SQUARE, LONDON, W.1.

*President:* Professor Frederic J. Cheshire, C.B.E., F.Inst.P.

*Hon. Secretaries:* Joseph E. Barnard, F.Inst.P., James A. Murray, M.D.

The section of the Society which has been formed to deal with the Industrial Applications of the Microscope, and to assist in the development of Industrial Research in British Industries, held a meeting on October 24.

#### PROGRAMME.

7.0 p.m.—Exhibits and Practical Demonstrations of new and improved instruments and apparatus of interest to those engaged in the Industries and to Microscopists generally.

8.0 p.m.—Communications:—

Professor F. J. Cheshire, C.B.E., P.R.M.S., presided.

MR. J. E. BARNARD, F.Inst.P., F.R.M.S., delivered the first of a series of Lecture Demonstrations, which embodied a practical course of instruction in the Manipulation of the Microscope. Detailed syllabus of these lecture demonstrations may be had on application.

Lecture 1.—The work-table of a microscopist who requires an ever-ready equipment. Illuminants suitable for various classes of work.

DR. MARIE C. STOPES, D.Sc., PH.D., F.L.S.: *The Microscopy of Recent Coal Research.*

Future meetings will be held as follows:

November 28: DR. SIDNEY H. BROWNING, L.R.C.P., M.R.C.S., F.R.M.S., *The Application of the Microscope to Industrial Diseases.*

January 23: SIR ROBERT A. HADFIELD, BART., D.Sc., F.R.S., F.INST.P., F.R.M.S., will preside.

CAPTAIN J. W. BAMFYLDE, *Some Failures in Steel as revealed by the Microscope and recorded by Photography.*

MR. H. B. MILNER, M.A., D.I.C., F.G.S., A.M.I.P.T., *The Use of the Microscope in the Petroleum Industry.*

#### GEOGRAPHICAL SOCIETY OF LONDON.

The next meeting of the Society will take place on Wednesday, November 7, at 5.30 p.m., when the following communications will be read:—

*On the Skeleton of IGUANODON ATHERFIELDENSIS sp. nov., from the Wealden Shales of Atherfield (Isle of Wight),* by the late REGINALD WALTER HOOLEY, F.G.S.

[Dr. A. Smith Woodward, F.R.S., has consented to read this paper, and, by kind permission of Mrs. Hooley, the skeleton of *I. atherfieldensis* will be exhibited in the meeting room. Dr. Smith Woodward will probably contribute some general remarks on the genus *Iguanodon*.]

*The Igneous Rocks of the Tortworth Inlier,* by PROF. S. H. REYNOLDS, M.A., Sc.D., F.G.S.

#### THE CHEMICAL SOCIETY.

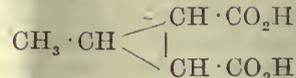
Papers read at the Ordinary Scientific Meeting, held on October 18:—

*The Chemistry of the glutaconic acids.* Part XV.: *Three-carbon tautomerism in the cyclopropane series.* Part 2. By F. R. GOSS, C. K. INGOLD, and J. F. THORPE.

Further experimental evidence was brought forward that the tautomeric relationship of the three isomeric esters of cyclic glutaconic acid is such that after the mobile hydrogen atom has passed into the carboxyl group, as in the enol-ester, it cannot return to the position which it takes up in the normal ester directly, but only by way of its position in the labile ester, *i.e.*, on the  $\alpha$ -carbon atom of the system, which

forms a halting place in the two stage migration.

In view of the apparent impossibility of reducing the acid to a saturated cyclopropane acid, the converse process has been studied. The acid



has been isolated in its three possible stereoisomeric modifications, and a double bond has been introduced into each. In each case the product is a cyclic glutaconic acid.

*Studies of Electrovalency.* Part III.: *The Catalytic Activation of Molecules and the Reaction of Ethylene and Bromine,* by R. G. W. NORRISH.

The hypothesis was advanced that molecular activation is at least partly a catalytic process consisting in the polarising of the reactant molecule by association with the molecule of a polar catalyst, either in a gaseous, surface, or liquid phase. Lowry's view that the molecules of unsaturated organic compounds which are unreactive in their resting form may become reactive by developing an electro-valence in the double bond, is a special form of this hypothesis in which the complete ionisation of the bond is postulated. The hypothesis was tested by investigating the reaction between ethylene and bromine. The dried gases practically ceased to react when enclosed by "non-polar" walls of paraffin wax, but reacted rapidly when enclosed by a "polar" surface of glass, stearic acid or cetyl alcohol. The reactivity of the gases as measured by the bimolecular velocity constant varies with the chemical nature of the enclosing surface, being greatest for stearic acid. On passing dry ethylene and bromine, diluted with air, through a paraffined tube, and then through a glass tube, no ethylene dibromide was observed in the paraffined tube, while about 0.3 gm. collected in the glass tube.

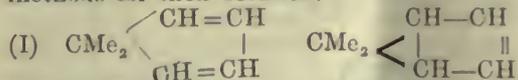
*Selenium Trioxide and Chloroselenic Acid,* by R. R. LE G. WORSLEY and H. B. BAKER.

The action of ozone on dry selenium had already been shown to produce only the dioxide, but by the use of a solvent this agent has carried the oxidation a stage further and selenium trioxide has been isolated. The solvent used was selenium oxychloride, which when alone was unaffected by ozone. The solution of selenium in the oxychloride showed little or no apparent change by treatment with 7 per cent. ozone for 30 hours, but after this the trioxide separated

out in considerable quantity. Analysis showed 62.01 per cent. of selenium,  $\text{SeO}_3$  requiring 62.26. The molecular weight by lowering of the freezing point of phosphorus oxychloride was found to be 136. Selenium trioxide is a very pale yellow powder of density 3.6. It decomposes at  $120^\circ$  without melting or subliming. It dissolves in water with evolution of heat, but is insoluble in ether and other common solvents. It combines directly with dry hydrogen chloride, producing chlorselenic acid, which is very similar to chlorsulphonic acid. Analyses and molecular weight determinations confirm the existence of the new acid.

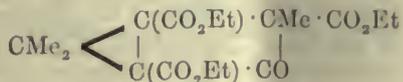
*The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides.* Part V.: *Orientation in the gem-dimethyl-dicyclopentane series*, by R. C. GRIMWOOD, C. K. INGOLD, and J. F. THORPE.

The proof adduced by recent experiments that derivatives of dimethylcyclopentadiene are tautomeric with corresponding derivatives of dimethyldicyclopentene, and that the nucleus of each substance of the series possesses two distinct phases which together confer on the compound a dual chemical character, raises certain problems of structure, principally relating to the orientation of attached groups, which require special methods for their solution.



Thus there are two positions in which the sodio-ester might methylate on carbon.

It was shown that the substance has formula



### PHYSICS IN THE TEXTILE INDUSTRIES.

The fifth of the series of public lectures on "Physics in Industry" being given under the auspices of the Institute of Physics will deal with this subject.

The lecture was delivered by Dr. A. E. Oxley, Physicist to the British Cotton Industries Research Association, at the Institution of Electrical Engineers, Victoria Embankment, London, on Monday, October 22, at 5.30 p.m.

The chair was taken by Sir Charles Parsons, K.C.B., F.R.S., who has just succeeded Sir J. J. Thomson as President of the Institute.

### CORRESPONDENCE.

#### DOES CANADA PREFER FRANCE?

(FROM LT.-COM. F. W. ASTBURY, M.P.)

To the Editors of THE CHEMICAL NEWS.

SIRS,—Before the Overseas Premiers return from the Imperial Conference to their various Dominions, it would be useful if we could all come to a clearer understanding about the policy underlying the Franco-Canadian Convention, which came into force at the beginning of last month. The effect of certain concessions made by Canada in that agreement to France has been to reduce the preference on British goods as compared with French, a trading advantage which at the moment is being very considerably emphasised by the cheapness of the franc.

The first result of the situation is most interesting. A syndicate of French manufacturers have already set up in Canada a dye-house where grey goods imported under the Convention may be coloured in the Dominion. A needless blow, that is to say, is being delivered, not only at our textile trades, but at British dyestuffs precisely when this young industry is taking the road to real prosperity.

The frank opinion of the Imperial Conference upon the whole question would certainly be illuminating. New Zealand's views would in particular be valuable, for there a "depreciated currency duty" has just been adopted to allow Britons a reasonable chance of competing for business in British markets.—Yours, &c.,

FRED W. ASTBURY.

14, St. Peter's Square, Manchester.

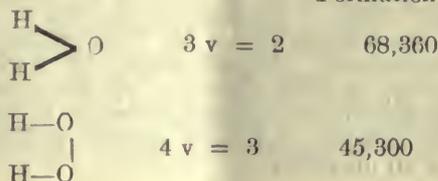
October 15, 1923.

#### PROPORTIONALITY AND HEAT OF FORMATION.

To the Editors of THE CHEMICAL NEWS.

SIRS,—Last year, Mr. Hawksworth Collins had a paper in *The Chemical News* (CXXV., 81 and 97), dealing with some thermo chemical data. In conjunction with some previous communications of mine, I would like to point out that the law he indicates is in application to compounds obtained as gases.

Heat of  
Formation.



In water, the change of volume on combining is one-third, the gas volumes are  $2 v H + 1 v O$ , and in hydrogen peroxide  $2 v H + 2 v O$ . Before combining, a gas volume 4 would become less on combination should hydrogen peroxide behave similarly to water, as its heat of formation indicates. Should the reduction in volume be, say, one-fourth, from the similarity of structure of the compounds and in four volumes,  $2 H + 2 O$  becoming  $3 v$  hydrogen peroxide, the product of molecular weight and change of volume is  $\frac{1}{4} \times 34 = 8.5$ ; in water it is  $\frac{1}{3} \times 18 = 6$ , and is sufficiently close in proportionality to the heats of these compounds as given in the above table.

It is sufficient to lend strong confirmation to the views expressed by Mr. Collins from the information in his table as applying to these compounds.—Yours, &c.,

J. C. THOMLINSON, B.Sc.

#### NOTICES OF BOOKS.

*Radio-Activity*, by K. FAJANS, Professor of Physical Chemistry in the University of Munich, translated by T. S. WHEELER, B.Sc., A.R.C.Sc.I., A.I.C., and W. G. KING. Pp. XII. + 138. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C.2. 1923. 8s. 6d. net.

The subject of Radio-Activity has developed, and is still developing so rapidly, that the treatises which gave the latest information on this Science a year or two ago are already incomplete. Prof. Fajans' volume, now translated into English by Messrs. Wheeler and King, although very complete in itself, comes as a kind of supplement to the earlier works on Radio-Activity.

The book, which is very readable and can be easily understood by all who possess an elementary knowledge of chemistry and physics, surveys the whole field of Radio-Activity. It opens with a study and classification of the Elements prior to the discovery of the radio-active transformations. The three radio-active series are then described, and an account is given of the chemical properties of the radio-elements.

There is also a short chapter on the Displacement Laws and their application. The significance of the isotopic varieties of lead as the end products of the disintegrations is emphasised. Recent important work on Isotopy in other elements, its detection by the positive ray method, attempts to separate isotopes and their general properties are all discussed.

Prof. Fajans has himself made many valuable contributions towards the elucidation of the phenomena of Radio-Activity, but he has largely confined himself to an exposition of the results of others, and his name does not even appear in the index. The importance of his Monograph may be gathered from the fact that it has gone through four editions in the original (the translation is based on the fourth German edition), and should pass through several English editions.

The translation has been well done, the illustrations have been well chosen, and the publishers have done their part well.

#### BOOKS RECEIVED.

*Kelly's Directory of the Chemical Industries*. Pp. XXX. + 903. 1923. Kelly's Directories, Ltd., 186, Strand, W.C.2. 30s.

*Treatise on General and Industrial Organic Chemistry*, by DR. ETTORO MOLINARI. Pp. VIII. + 457 to 897. Second English Edition, Part II. 1923. Messrs. J. & A. Churchill, 7, Great Marlborough Street, W.1. 30s. net.

*The Electron in Chemistry*, by SIR J. J. THOMSON, O.M., F.R.S. Pp. 144. 1923. J. B. Lippincott Company, Philadelphia.

*The Expert Witness*, by C. A. MITCHELL, M.A., F.I.C. Pp. XV. + 188. 1923. Messrs. Heffer & Sons, Ltd., 4, Petty Cury, Cambridge. 7s. 6d. net.

### New Patents.

This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

24495—Farbenfabriken vorm. F. Bayer & Co.—Manufacture of silicic acid gels. Oct. 2.

24367—King, P. H.—Method of retarding oxidation in gums and resins. Oct. 1.

24477—Monterumici, R.—Preparation of magnesia hydrate. Oct. 2.

#### Specifications Published this Week.

204223—McDougall, I., and Howles, F.—Process for the manufacture of lead arsenate.

192376—National Aniline & Chemical Co., Inc.—Alkylation and aralkylation of carbazol.

197690—Soc. d'Etudes Chimiques Pour l'Industrie.

#### Abstract Published this Week.

amide of manures containing soluble organic nitrogen.

203709—Jouve, A. J. B., Helbronner, A., and Soc. Hydro-Electrique & Metallurgique du Palais.—Manufacture of chromates and bichromates.

—Process for the manufacture from cyan-  
202016—Lignone derivatives; cellulose; sulphurous acid.—Cross, C. F., of 3, New Court, Lincoln's Inn, London, and Engelstad, A., of Vardol, Norway.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3316.

## ARE THE NATURAL GROUPINGS OF THE ELEMENTS AND THE SPECTRAL LINES OF HYDROGEN RELATED?

PART II.

By F. H. LORING.

In this Journal of October 26, 1923, pages 257-259, the subject as indicated by the above title was tentatively discussed, it being shown that the  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$  series lines of hydrogen were directly related to certain natural groups and groupings of the elements represented by a series of five numbers, so that from these emission lines the said numbers could be derived. It is proposed to designate these groups and groupings by the above Greek letters, as shown in the scheme at the conclusion of this part of the paper. The scheme also serves to summarise the main features involved in this study.

The subject merits wider treatment, as, indeed, in principle it is a very interesting problem. Before, however, probing the matter further, the following corollary may be noted:—If the relationship in question holds, then one could say with some truth that the law of the part is the law of the whole, and therefore the hydrogen atom is a part of every element taken in the atomic sense; and Prout's hypothesis is true. The word *is* in this statement may carry an added meaning, such as, *is convertible into*.

Prof. Eddington, in his "Mathematical Theory of Relativity," gives expression to a significant idea, viz.: "This suggests striving for an ideal—to show, not that the laws of nature come from a special construction of the ultimate basis of everything, but that the same laws of nature would prevail for the widest possible variety of that basis."

This statement seems to be very significant, but be this as it may, the relationship shown clearly indicates that if it is true, then it should be the means of finding further interesting relations between the spectrum of hydrogen and the elements taken collectively. This, in fact, has been the case in a general way quite apart from this particular relation, as is instanced in the energy levels of an atom which become realised in other atoms by bombarding

them with electrons. It must be remembered, too, that in the electron orbits of the hydrogen atom the major axes of the ellipses traced out in space are related to each other as the squares of numbers 1, 2, 3, &c., are; and, moreover, the X-ray spectra of the elements as found by Moseley stand in uniform step-wise relationship if the frequencies of the lines of the elements, taken consecutively according to their atomic numbers, are re-proportioned by taking respectively their square roots. In conformity with these relations the atomic numbers grow progressively by steps of one each time, beginning with hydrogen, and "the difference between the atomic weight [individual mass value] and the atomic number represents the number of electrons there must be in the nucleus [of the atom] in order to bring its net charge down to the atomic number"—to quote the words of B. Russell in his "A.B.C. of Atoms."

Furthermore, the Kossel-Sommerfeld law, which shows similar inner structures of the atom to be common to consecutive elements, means that a common type or system of atom building is involved, and from the foregoing this implies that hydrogen is the smallest positive unit in the architectural structure of the atom. Sommerfeld, in his "Atomic Structure and Spectral Lines," page 373, says: "We next assert that the spark spectrum of each element is in structure the same as the arc spectra of the element that precedes it in the periodic system; that is, that it consists of doublet, triplet, or so-called non-series lines, according as the arc spectrum of the preceding element is composed of doublets (like the alkalis), or triplets (like the alkaline earths), or of lines that apparently succeed one another without regularity (like most elements at the right of the periodic system, in particular the inert gases). Here we have enunciated the [Spectral] Law of Displacement, which, like the law of displacement of radio-activity, leads from one element of the periodic system to a neighbouring element. The meaning of our displacement law as applied to our model of the atom is obvious. Each column of the periodic system is, in general language, characterised by a certain valency; or, in our model, by a certain number of external electrons. On the other hand, we know that the line-structure of the spectra is, without exception, the same in each column of the series. If, now, the atom loses one electron by ionisation, then it becomes a member of the preceding column in its external behaviour,

and thus, as our law of displacement asserts, it will conform in the structure of its lines with the members of the preceding column; numerically, it will be best comparable with the element that immediately precedes it in the periodic system."

Enough has been said here to show how intimately the elements (atoms) are structurally connected; and whether the inert gases are allocated to the right or to the left of the table makes no real difference, since the table has to be considered as developed continuously. This continuity is shown by the radio-atoms which, in their change from one type to another, pass right across the table. The inert gases are, however, quite distinctive, as may be judged from the above quotation, especially when taking other factors into account. The grouping of the elements is a natural procedure, and it seems to have a certain counterpart in the line spectrum of hydrogen, as already indicated.

Considering the hydrogen lines, it is known that those made use of in this study are not in one sense pure lines, but that they are made up of fine-line companions. For example, the H<sub>α</sub> line appears to have a certain complexity, which Sommerfeld has attributed to a relativity effect, since, according to this theory, the elliptical orbits rotate in their own planes, the nucleus occupying one foci—just as the

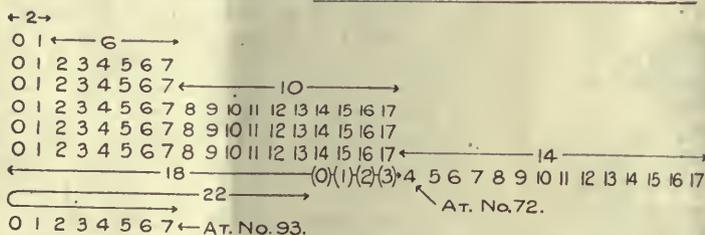
planet Mercury describes an elliptical orbit round the sun, and it turns slowly in its own plane round this luminary as the pivot. The ellipse in this case is not a mathematically closed one, but it becomes a sort of elliptical spiral. The calculated wave lengths for the above line when reduced to vacuum figures are as follows:—

H<sub>α</sub> Line.

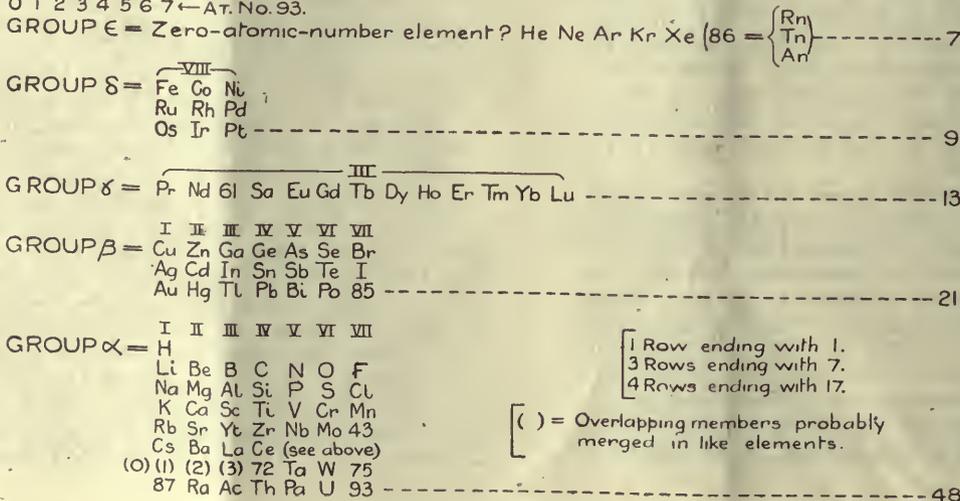
6564.501
0.516
0.563
0.658
0.674
0.720

Apart from this ultra refinement, these Balmer series lines made use of in this study stand out in strong contrast to the general "background," by reason of their marked intensities. These intensities (B) taken advisedly from W. M. Watt's "Study of Spectra Analysis," 1904, p. 230, do not give an adequate idea of their development as now understood, but they will serve a general purpose of comparison with the corresponding group numbers (A), thus:—

A	B
48	20 α
21	20 β
13	15 γ
9	10 δ
7	8 ε



$$\begin{aligned} 2+4 &= 6 \\ 6+4 &= 10 \\ 10+4 &= 14 \\ 14+4 &= 18 \\ 18+4 &= 22 = \text{LIMIT.} \end{aligned}$$



- 1 Row ending with 1.
- 3 Rows ending with 7.
- 4 Rows ending with 17.

( ) = Overlapping members probably merged in like elements.

Numbers derived from the Balmer line emission spectrum of hydrogen, being lines: α, β, γ, δ, ε.

Interesting developments in connection with the hydrogen lines seem to be foreshadowed, but of more immediate interest may be the following scheme which gives at a glance the group system evolved by reason of this study.

#### NOTES RESPECTING THE SCHEME.

Referring to the wedge periodic table (see *The Chemical News*, 1922, CXXV., p. 387; or the writer's "Atomic Theories," 2nd Edition, frontispiece; or the writer's "The Chemical Elements," pages 34, 107-110), which conforms with the above lay-out in every respect, Mn is on a lower level than Cl; similarly, Ce is on a lower level than Zr, while the element 72 (cerium or hafnium) rises to the level of Zr. This also suggests that the overlapping at this part of the table is to be expected. The overlapping extension, moreover, accounts for the tendency of a zero-valency member to appear in this part of the table, as has been the case with some of the earlier schemes. Sir J. J. Thomson claims to have found an inert gas of atomic weight 163, but this is doubtful, though the (0) member falls at about 167. See the writer's "The Chemical Elements," pages 149, 150. Referring now to H, this being on a short steep wedge, as already explained in Part I., it is raised to the level of F. Considering the "7" and "17" elements at the highest part of the wedges, they are chemically alike, as instanced in the halogens which occupy these extreme places as far as filled. 93 represents a lacuna not filled, for it is based upon a minimum-production limiting-series (see *The Chemical News*, 1922, CXXV., p. 309), thus:—

	At. No.	Diff.
	93	—
	Pa = 91	2
		6
	85	10
	75	14
	61	18
	43	22
	Sc = 21	

The small amount of Se compared with Ca and Ti on each side of Sc supports this observation; and it will be seen that the series becomes a limiting one by reason of the values of the differences shown. There appears to be comparatively small quanti-

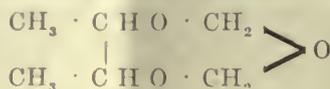
ties of Pa, and UX<sub>2</sub> which is an isotope, when considering the surrounding elements. The radio-isotopes, of course, are included in the atomic-number places characterised by the elements Ra, Ac, Th, &c.

#### DIACETYL ACETONE AND PSEUDO-CUMENE.

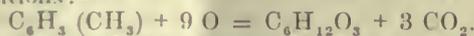
By J. C. THOMLINSON, B.Sc.

A table giving all the proposed formulae for diacetyl acetone would be too cumbersome in a short note of this kind.

The following ring structure,



is advanced for this substance, since it may be obtained by the oxidation of pseudo-cumene with chromic under suitable conditions:—



This oxidation is similar to that which takes place when alcohols are oxidised by chromic acid.

#### THE SALTS OF MALEIC, FUMARIC AND INACTIVE MALIC ACIDS.

By JOHN MORRIS WEISS AND CHARLES RAYMOND DOWNS.

(From the "Journal of the American Chemical Society," October, 1923.)

In various investigations which had for their purpose the development of analytical methods for mixtures of maleic, fumaric and malic acids, a number of salts of these three acids were prepared and studied. The results are admittedly incomplete, and in certain instances the compounds deserve further study. We are presenting here the results obtained, regretting that we did not have the time to study all the compounds thoroughly, but hoping that others will do so. We wish to express our thanks to Dr. G. C. Bailey, Dr. H. E. Williams, and Dr. Wolesensky, for the careful work which they carried on under our direction in preparing and determining the formulae and solubilities of a number of the compounds described, and to Mr. E. C. Buck for the very careful preliminary search of the literature which he made in this connection.

## AMMONIUM SALTS.

*Analysis.*—These salts were analyzed by distilling the material with an excess of standard sodium hydroxide solution and collecting the distillate in an excess of standard sulphuric acid. The distillate, titrated back with methyl orange as indicator, gave the ammonia content; and the flask residue, titrated back with phenolphthalein as indicator, gave the acid radical content.

*Ammonium Fumarate.*<sup>1</sup>—The product was best prepared by treating fumaric acid suspended in water with concd. ammonium hydroxide in slight excess of the calculated amount, concentrating in a vacuum at not over 60°, adding a little ammonium hydroxide to make up for losses in concentration and allowing the substance to crystallize. The crystals were filtered and washed with alcohol.

*Analyses.*—Calc. for  $(\text{NH}_4)_2\text{C}_4\text{H}_2\text{O}_4$ :  $\text{NH}_3$ , 2.67;  $\text{C}_4\text{H}_4\text{O}_4$ , 77.33. Found:  $\text{NH}_3$ , 22.55;  $\text{C}_4\text{H}_4\text{O}_4$ , 77.40.

The aqueous solution of the salt is stable at 60°, but when boiled it loses ammonia; 4.5506 g. of salt was dissolved in 200 cc. of water and the solution distilled, the distillate being collected in standard acid. In 50 minutes 0.08148 g. of ammonia distilled with 150 cc. water, representing 7.9 per cent. decomposition. On the addition and distillation of 150 cc. more water, 0.03933 g. of ammonia was volatilized (3.8 per cent.). The final limit of this decomposition or the product formed was not determined.

*Ammonium Acid Fumarate.*<sup>2</sup>—Fumaric acid was neutralized by two molecules of ammonium hydroxide with litmus as indicator and a second portion of fumaric acid equal to the first added. The mixture was fractionally crystallized into two lots of crystals, each equivalent to slightly more than  $\frac{1}{3}$  of the whole, the balance in the mother liquor being discarded.

*Analyses.*—Calc. for  $\text{NH}_4\text{C}_4\text{H}_3\text{O}_4$ :  $\text{NH}_3$ , 12.78;  $\text{C}_4\text{H}_4\text{O}_4$ , 87.21. Found: Fraction 1:  $\text{NH}_3$ , 11.70;  $\text{C}_4\text{H}_4\text{O}_4$ , 87.70; Fraction 2:  $\text{NH}_3$ , 12.70;  $\text{C}_4\text{H}_4\text{O}_4$ , 87.40.

*Ammonium Maleate.*<sup>1, 3</sup>—We were not able to obtain crystalline material by the same method as that used for ammonium fumarate. Under ordinary pressure, the solution does not lose ammonia by evapora-

tion. Only a thick sirup results which cannot be crystallized. When the solution is evaporated in a vacuum, the solid obtained is ammonium acid maleate. This salt deserves attention by future investigators.

*Ammonium Acid Maleate.*<sup>3</sup>—This salt was obtained by the same method as described under the corresponding fumarate.

*Analyses.*—Calc. for  $\text{NH}_4\text{C}_4\text{H}_3\text{O}_4$ :  $\text{NH}_3$ , 12.78;  $\text{C}_4\text{H}_4\text{O}_4$ , 87.21. Found:  $\text{NH}_3$ , 17.72;  $\text{C}_4\text{H}_4\text{O}_4$ , 87.16.

## SODIUM SALTS.

The sodium acid maleate<sup>3, 4</sup>, sodium maleate<sup>3, 4</sup>, sodium acid fumarate<sup>5</sup> and sodium fumarate<sup>2, 5, 6</sup> were prepared by mixing the acids with the proper amounts of sodium hydroxide in water solution, allowing the salt to crystallize and drying it at room temperature.

The data on water of crystallization as given in the literature were confirmed by ignition to sodium carbonate. In the case of the sodium acid fumarate, where there are no data, we found the crystalline material to be anhydrous.

## BARIUM AND STRONTIUM SALTS.

Barium acid maleate,<sup>3</sup> barium maleate,<sup>3, 7, 8</sup> barium fumarate<sup>2</sup> and barium *i*-malate,<sup>9, 10, 11</sup> have been described. We did not isolate these, but observed that a heavy white precipitate of slight solubility was obtained when a 10 per cent. solution of barium chloride was added to a 10 per cent. solution of either sodium maleate or fumarate. With sodium *i*-malate only a slight precipitate was formed.

Strontium acid maleate and strontium maleate<sup>3</sup> and strontium *i*-malate<sup>11</sup> have been prepared.

Strontium fumarate<sup>2</sup> has been described as containing three molecules of water of crystallization.

We prepared this salt by mixing strontium nitrate and sodium fumarate in water

<sup>4</sup> Bodewig, *Z. Kryst.*, 1881, V., 558.

<sup>5</sup> Chandler, *Jour. Am. Chem. Soc.*, 1908, XXX., 694.

<sup>6</sup> Kannonikov., *J. prakt. Chem.*, 1885, [2], XXXI., 321.

<sup>7</sup> Kekulé and Strecker, *Ann.*, 1884, CCXXIII., 170.

<sup>8</sup> Vorlaender, *Ann.*, 1894, CCLXXX., 177.

<sup>9</sup> Kekulé, *Ann.*, 1861, CXVII., 120.

<sup>10</sup> Buisine, *Compt. rend.*, 1888, CVI., 1426.

<sup>11</sup> Duboux and Cuttat, *Helvetica Chim. Acta*, 1921, IV., 735.

<sup>1</sup> Keiser and McMaster, *Am. Chem. J.*, 1913, XLIX., 84.

<sup>2</sup> Ricckher, *Ann.*, 1844, XLIX., 31.

<sup>3</sup> Buechner, *Ann.*, 1844, XLIX., 57.

solution in equimolecular proportions, filtering off the precipitate and drying at 100° at which temperature it was anhydrous.

*Analyses.*—Calc. for  $\text{SrC}_4\text{H}_2\text{O}_4$ : Sr, 43.45; H, 0.99. Found: Sr, 43.25; H, 1.13.

#### CALCIUM SALTS.

The compositions were determined by igniting the salts to calcium oxide.

*Calcium Acid Maleate*<sup>3</sup> was prepared and found to correspond with the formula as given for 5 molecules of water of crystallization. With the neutral salt<sup>3</sup> the same coincidence was observed, this salt containing one molecule of water.

*Analysis.*—Calc. for  $\text{CaC}_4\text{H}_2\text{O}_4 \cdot \text{H}_2\text{O}$ : Ca, 23.25. Found: 23.28.

*Calcium Fumarate*<sup>2, 7, 12</sup> was prepared by precipitating a sodium fumarate solution with calcium chloride, and filtering, washing and air-drying the product. Our material corresponded to the trihydrate described in the literature.

*Analyses.*—Calc. for  $\text{CaC}_4\text{H}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ : Ca, 19.23; H, 3.84. Found: Ca, 19.47; H, 4.01.

*Calcium Acid Fumarate* is not described in the literature. When a solution of sodium acid fumarate was mixed with a molecular equivalent of calcium chloride and evaporated, crystals were obtained which were separated and air-dried.

*Analysis.*—Calc. for  $\text{CaC}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ : Ca, 13.06. Found: 13.22.

*Calcium Acid i-Malate*<sup>13</sup> is stated to contain one molecule of water of crystallization. Our preparation was made by heating 52.8 g. of i-malic acid with 20 g. of calcium carbonate, filtering the solution, allowing it to crystallize, and separating and air-drying the crystals; yield, 64 g. The substance was found to be the anhydrous salt.

*Analysis.*—Calc. for  $\text{CaC}_4\text{H}_8\text{O}_8$ : Ca, 13.06. Found: 12.85.

#### MAGNESIUM SALTS.

Magnesium acid maleate, magnesium maleate,<sup>3, 14</sup> magnesium fumarate<sup>2</sup> and magnesium i-malate<sup>11</sup> have been described. These salts were not prepared, but note was made that none of the three acids is precipitated from its sodium salt solutions (10 per cent.) by soluble magnesium compounds. In an attempt to produce the i-

malate, magnesium oxide was dissolved in i-malic acid. On concentrating the filtered solution a syrup was obtained which did not crystallize, but solidified on standing to a hard white mass.

#### COBALT SALTS.

*Cobalt Maleate* is not described in the literature.

Cobalt was precipitated as carbonate from a solution of its nitrate and the latter filtered, washed and suspended in water. An equivalent quantity of maleic acid was added and the solution filtered and evaporated.

*Analysis.*—Calc. for  $\text{CoC}_4\text{H}_2\text{O}_4 \cdot 11\text{H}_2\text{O}$ : Co, 15.90. Found:<sup>15</sup> 15.80.

*Cobalt Fumarate*<sup>2</sup> is stated to correspond to the formula  $\text{CoC}_4\text{H}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ ; this we were unable to confirm. Using concentrated solutions of cobalt nitrate and sodium fumarate, a copious, crystalline, pink precipitate was obtained. This was washed and air-dried.

*Analyses.*—Calc. for  $\text{CoC}_4\text{H}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ : C, 19.59; H, 4.08; Co, 24.07. Found: C, 20.36; H, 3.86; Co, 23.93.

When the pink compound was dried at 100° it became somewhat bluish from loss of water.

*Analysis.*—Calc. for  $\text{CoC}_4\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ : Co, 28.23. Found: 28.62.

*Cobalt i-Malate.*—This is not described in the literature. It was prepared by treating cobalt carbonate suspended in water with the calculated amount of i-malic acid and evaporating the mixture to dryness at 100°. The formula seems to be that of a trihydrate.

*Analyses.*—Calc. for  $\text{CoC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ : C, 4.08; H, 24.07; Co, 19.59. Found: C, 4.15; H, 23.40; Co, 19.28.

#### NICKEL SALTS.

The nickel was determined by digesting a sample with concentrated ammonium hydroxide, adding water, a small amount of sodium iodide (0.02–0.05 g.), a few drops of standard silver nitrate solution and an excess of standard sodium cyanide solution. The excess was titrated back with silver nitrate to a slight permanent precipitate.

*Nickel Fumarate*<sup>2</sup> is stated to contain 4 molecules of water of crystallization. The salt was prepared by mixing dilute solutions of nickel nitrate and sodium fumarate and concentrating until a green crystalline pre-

<sup>12</sup> *Carius, Ann.*, 1867, CXLII., 129.

<sup>13</sup> *Bremer, Ber.*, 1875, VIII., 863.

<sup>14</sup> *Walden, Z. physik. Chem.*, 1897, I., 529.

<sup>15</sup> *Cobalt was determined by ignition to cobaltous cobaltic oxide, Co<sub>3</sub>O<sub>4</sub>.*

precipitate was formed, and removing soluble materials by repeated boiling with water.

*Analyses.*—Calc. for  $\text{NiC}_4\text{H}_2\text{O}_4 \cdot 4\text{H}_2\text{O}$ : Ni, 24.08; calc. for  $\text{NiC}_4\text{H}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ : 22.43. Found: 23.42.

If the precipitation of the nickel fumarate is carried on in concentrated solution, a different product seems to be formed.

*Analyses.*—Calc. for  $\text{NiC}_4\text{H}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ : C, 18.27; H, 4.56; Ni, 22.43. Found: C, 18.44; H, 4.06; Ni, 22.30.

*Nickel Maleate*<sup>3</sup> resembles the fumarate in general properties, but appears to be more soluble. This compound was not analyzed.

*Nickel i-Malate* is not described in the literature. It is extremely soluble in water and, therefore, cannot be precipitated. If nickel carbonate is dissolved in malic acid a green solution is obtained, which, on concentration, forms a jelly. On long standing at room temperature, the sample lost water and crystals began to appear. This compound was isolated but not analyzed.

#### MANGANOUS SALTS.

*Manganous Acid Maleate.*—This compound has not been previously described; 69.6 g. of maleic acid was dissolved in the minimum amount of water at 30°, and to this was added 34.6 g. of manganese carbonate. A solid separated which was dissolved by warming it. As the solution was cooled in ice water, a granular pink precipitate was formed which was filtered, washed, recrystallized from water, and dried at room temperature; yield, 32.5 g.

*Analyses.*—Calc. for  $\text{MnC}_8\text{H}_6\text{O}_8 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ : C, 25.60; H, 4.20; Mn, 15.02. Found: C, 25.37; H, 3.91; Mn, 15.19.

From examination of the crystals microscopically, it appears that the salt is stable in the air and in a vacuum over sulphuric acid.

*Manganous Maleate* has not been previously described. It was prepared in the same manner as the acid salt, except that twice as much manganese carbonate was used. It appears to be stable at 100°. In dil. water solution it decomposes with the formation of manganese dioxide.

*Analyses.*—Calc. for  $\text{MnC}_4\text{H}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ : C, 21.53; H, 3.58; Mn, 24.64. Found: C, 21.01; H, 3.31; Mn, 24.48.

*Manganous Fumarate*<sup>2</sup> has been stated to have the formula  $\text{MnC}_4\text{H}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ . Our results did not confirm this. To 11.55 g. of manganese carbonate we added 11.6 g. of fumaric acid. The slight excess of carbonate was filtered off and the filtrate eva-

porated until a precipitate appeared, at first flocculent and then granular. This was filtered off and dried at room temperature.

*Analyses.*—Calc. for  $\text{MnC}_4\text{H}_2\text{O}_4$ : C, 28.41; H, 1.18; Mn, 32.54. Found: C, 27.55; H, 1.42; Mn, 32.02.

#### ZINC SALTS.

Zinc was determined by ignition to zinc oxide.

*Zinc Acid Maleate*<sup>16</sup> was not prepared.

*Zinc Maleate*<sup>3</sup> was made by quickly mixing a saturated maleic acid solution with zinc carbonate as a paste in a mortar and filtering before the zinc maleate separated. Zinc maleate formed as a white, granular precipitate which was washed and dried at room temperature.

*Analyses.*—Calc. for  $\text{ZnC}_4\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ : C, 22.80; H, 2.78; Zn, 30.42. Found: C, 21.78; H, 2.78; Zn, 30.68.

When a solution of zinc maleate is heated, it decomposes giving a flocculent precipitate.

*Zinc Fumarate*<sup>2</sup> has been described in two modifications with 3 and 4 molecules of water, respectively. Our product was made by treating a suspension of fumaric acid with an excess of zinc carbonate in a mortar, filtering the mixture and evaporating the filtrate until crystallization began. Colourless crystals were obtained and dried at room temperature.

*Analyses.*—Calc. for  $\text{ZnC}_4\text{H}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ : C, 17.81; H, 4.45; Zn, 24.26. Found: C, 17.24; H, 4.25; Zn, 24.42.

#### IRON SALTS.

*Ferric Maleate*<sup>3</sup> has been described as an indeterminate smear. On evaporation of a mixture of two molecular equivalents of ferric hydroxide and three molecular equivalents of maleic acid a dark, nearly black, amorphous mass was obtained which was dried at 100°. When analyzed this showed approximately the composition of the dihydrate.

*Analyses.*—Calc. for  $\text{Fe}_2(\text{C}_4\text{H}_2\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$ : C, 29.4; H, 2.04; Fe, 22.88. Found: C, 27.34; H, 2.59; Fe, 22.90.

In solution this material seems to be able to hold an excess of ferric hydroxide.

*Ferric Fumarate*<sup>2</sup> could not be prepared from ferric hydroxide and fumaric acid.

*Ferric i-Malate*<sup>17</sup> was not prepared, but considerable work was carried on with *ferric*

<sup>16</sup> Richter, *Z. Chem.*, 1868, XI., 449.

<sup>17</sup> Pickering, *J. Chem. Soc.*, 1914, CIII., 1358.

*ammonium i-malate*. One molecular equivalent of ferric hydroxide (precipitated cold because when precipitated hot it did not dissolve properly) was mixed with a clear solution of 2 molecular equivalents of malic acid and the mixture was heated to 60°. One molecular equivalent of ammonium hydroxide was then added, and the mixture heated rapidly to boiling. The work was carried on in semi-darkness as the material is light sensitive. A clear, red-brown solution resulted which was cooled rapidly in an ice-bath. It showed no ferrous iron when tested with ferricyanide solution. The solution was not stable even in the dark, as ferrous iron appeared on standing and gradually increased. When a thick solution was painted on glass and dried in a dark closet at room temperature a solid similar to ferric ammonium citrate was produced which contained no ferrous iron. When it was dried between 30° and 40° some reduction took place.

To compare the sensitivity of ferric ammonium malate and citrate, dilute solutions of each, free from ferrous iron, were placed in sunlight and tested for ferrous iron. After 5 minutes the malate showed a faint test for ferrous iron and after 10 minutes a very positive test, while the citrate was negative at 24 minutes and showed a positive test only after 39 minutes. In the dark at 100° after 5 minutes the malate showed ferrous iron, while after 20 minutes the citrate still tested negatively.

Attempts to produce ferric ammonium maleate or fumarate in the same way were unsuccessful.

#### COPPER SALTS.

Copper was estimated volumetrically in acetic acid solution by means of sodium iodide and thiosulphate.

*Copper Fumarate*<sup>2 12 18</sup> has been described both as a dihydrate and trihydrate. We obtained our material by precipitating fumaric acid with copper sulphate. The pale blue precipitate was washed and dried at 100°.

*Analyses*. — Calc. for  $\text{CuC}_4\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ : C, 22.47; H, 2.80; Cu, 29.78. Found: C, 21.70; H, 3.06; Cu, 29.45.

*Copper Maleate*<sup>3 18</sup> was prepared by precipitating a solution of equimolecular equivalents of copper sulphate and maleic acid with sodium carbonate. A deep blue crys-

talline precipitate formed which, as stated by the previous investigators, is the monohydrate.

*Analyses*.—Calc. for  $\text{CuC}_4\text{H}_2\text{O}_4 \cdot \text{H}_2\text{O}$ : C, 24.54; H, 2.04; Cu, 32.50. Found: C, 24.05; H, 2.39; Cu, 32.22.

*Copper i-Malate* has not been described. When equivalent quantities of copper carbonate and *i*-malic acid solutions are mixed and the mixture is evaporated, a hard vitreous blue mass is formed, which after several weeks becomes crystalline. It contains at this stage 25.02 per cent. of copper, which indicates a trihydrate (25.49 per cent. of copper). On continued exposure, the mass becomes paler blue and shows the presence of 25.70 per cent. of copper.

*Analyses*. — Calc. for  $\text{CuC}_4\text{H}_4\text{O}_5 \cdot 2\text{H}_2\text{O}$ : C, 20.72; H, 3.45; Cu, 27.28. Found: C, 20.86; H, 3.16; Cu, 25.70.

This formula is quite doubtful and further work is indicated.

#### CADMIUM SALTS.

Cadmium salts of maleic and fumaric acids have not been described in the literature. Cadmium was determined by igniting the salt to the oxide, CdO, in a stream of oxygen.

*Cadmium Fumarate*.—Prepared by precipitating sodium fumarate with cadmium chloride in concentrated solutions this forms a copious, finely divided, white precipitate. It was filtered, washed and dried at 100°.

*Analyses*. — Calc. for  $\text{CdC}_4\text{H}_2\text{O}_4$ : C, 21.20; H, 0.88; Cd, 49.57. Found: C, 21.63; H, 1.18; Cd, 49.29.

*Cadmium Maleate*.—This was made by mixing equimolecular proportions of cadmium chloride and sodium maleate in solution and evaporating to crystallization. The salt was washed repeatedly with hot water and dried at room temperature.

*Analyses*. — Calc. for  $\text{CdC}_4\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ : C, 18.29; H, 2.28; Cd, 42.75. Found: C, 17.76; H, 2.27; Cd, 42.50.

The salt retains sodium chloride tenaciously and needs exhaustive washing to purify it.

#### ANTIMONY SALTS.

No literature references were found to these salts, and all attempts to form the maleate, fumarate or *i*-malate by dissolving antimony trioxide in the corresponding acid were unsuccessful. In the case of *i*-malate, some oxide is dissolved (never more than 21 per cent. of that calculated), but apparently

<sup>18</sup> Pickering, *J. Chem. Soc.*, 1912, CI., 174.

an excess of acid is required to prevent hydrolysis so that the salt cannot be isolated.<sup>19</sup>

*Sodium Antimonyl i-Malate*.—Attempts were made to prepare this salt by heating 40 g. of sodium hydroxide, 144 g. of antimony trioxide and 134 g. of *i*-malic acid in water solution under a reflux condenser. After 15 hours, 82.8 g. of antimony trioxide remained undissolved. This was removed, dissolved in potassium acid tartrate and reprecipitated, washed and added again to the mixture. In this way all but 31 g. of the original quantity was finally dissolved, and all attempts to increase this failed. The final solution was evaporated to a thick syrup which, on seeding, solidified to a white, hard mass. It can be powdered, and is apparently stable and very soluble in water. The problem of these complex salts is interesting and deserves further work.

#### LEAD SALTS.

Lead was determined gravimetrically as the chromate or by titrating excess of dichromate with sodium iodide and thiosulphate.

*Lead Fumarate*<sup>2</sup> is stated to occur as the dihydrate. When equimolar quantities of lead nitrate and sodium fumarate were mixed in aqueous solution, fine crystalline flakes were obtained which were filtered and dried at 100°.

*Analyses*.—Calc. for  $\text{PbC}_4\text{H}_2\text{O}_4$ : C, 14.91; H, 0.62; Pb, 64.48. Found: C, 14.48; H, 0.88; Pb, 64.22.

*Lead Maleate*<sup>3 20</sup> is stated to occur as the trihydrate. When we prepared it in a manner similar to that used for the fumarate, we obtained the anhydrous salt.

*Analyses*.—Calc. for  $\text{PbC}_4\text{H}_2\text{O}_4$ : C, 14.91; H, 0.62; Pb, 64.47. Found: C, 14.94; H, 0.78; Pb, 64.20.

*Lead i-Malate*<sup>21</sup> is the subject of varying opinion, being reported as anhydrous, with  $1\frac{1}{2}$  molecules water and with 3 molecules water. This salt was obtained as a white precipitate by interaction of lead nitrate and sodium *i*-malate in aqueous solution. When heated to 100° it softens to a dough-like mass. Its formula is doubtful but seems to

<sup>19</sup> Henderson and Barr, *J. Chem. Soc.*, 1896, LXIX., 1451. Henderson and Prentice, *ibid.*, 1894, LXVII., 1030.

<sup>20</sup> Pelouze, *Ann.*, 1834, XI., 263.

<sup>21</sup> Lloyd, *Ann.*, 1878, CXCII., 80. Kekulé, *Ann.*, 1864, CXXX., 1. Pasteur, *Ann. chim.*, 1852 [3] XXX., 49. Werigo and Tanatar, *Ann.*, 1874, CLXXIV., 367.

approach the composition  $\text{PbC}_4\text{H}_4\text{O}_5 \cdot \frac{1}{2}\text{H}_2\text{O}$ .

*Analyses*.—Calc. for  $\text{PbC}_4\text{H}_4\text{O}_5 \cdot \frac{1}{2}\text{H}_2\text{O}$ : C, 13.78; H, 1.43; Pb, 59.48. Found: C, 11.91; H, 1.46; Pb, 59.42.

#### SILVER SALTS.

Silver was determined as the chloride.

*Silver Maleate*<sup>3 7</sup>.—This was formed by precipitating silver nitrate solution with sodium maleate and was obtained as a white precipitate which was dried at 100°.

*Analysis*.—Calc. for  $\text{Ag}_2\text{C}_4\text{H}_2\text{O}_4$ : Ag, 65.42. Found: 65.44.

The compound deflagrated when heated during combustion (leaving metallic silver) and the carbon and hydrogen results are considered unreliable.

*Silver Fumarate*.—This compound has not been described. It was prepared in the same way as was the maleate, and behaved similarly. Its silver content was 64.90 per cent.

#### SOLUBILITIES.

A number of the salts were tested for solubility in water. Samples were placed in 60 cc. bottles with distilled water and securely stoppered. They were then held in a thermostat at the required temperature for 24 hours, 25 cc. portions of the clear solutions were withdrawn in a weighing bottle by means of a pipet with cotton filter, weighed, transferred to a platinum dish, evaporated to dryness and heated to constant weight at 100°. With the acid salts, the amount of solute was determined by titration. The sampling of the solutions saturated at 60° and 100° was done entirely under the surface of the water in the thermostat with an apparatus described by Pawlewski.<sup>22</sup>

The solubility results are given in Table I.

#### SUMMARY.

The data in the literature regarding the salts of maleic, fumaric and *i*-malic acids have been reviewed and the water of crystallization of a number of these salts determined. In some cases the work agrees with that of past observers, but in others new numbers are apparently justified. Some 11 salts, not previously described, were prepared and the water of crystallization determined in certain cases definitely.

The solubilities in water of 22 salts were determined and tabulated. In general, fumarates are less soluble than the corresponding maleates.

50, East 41st Street, New York, N.Y.

<sup>22</sup> Pawlewski, *Ber.*, 1899, XXXII., 1040.



TABLE I.

SOLUBILITIES OF FUMARATES, MALEATES AND MALATES.		Solubilities in g. per 100 g. of water.				
Compound.	Formula.	25°	30°	40°	60°	100°
Cadmium fumarate ..	$CdC_4H_2O_4$	...	0.09	...	...	...
Cadmium maleate ....	$CdC_4H_2O_4 \cdot 2H_2O$	...	0.66	...	...	...
Calcium acid fumarat	$Ca(C_4H_4O_4)_2 \cdot 2H_2O$	...	5.19	...	...	...
Calcium fumarate ....	$CaC_4H_2O_4 \cdot 3H_2O$	...	1.56	...	...	...
Calcium acid maleate	$Ca(C_4H_3O_4)_2 \cdot 5H_2O$	21.13	...	41.89	94.78	...
Calcium maleate .....	$CaC_4H_2O_4 \cdot H_2O$	2.49	...	2.88	...	...
Cobalt fumarate .....	$CoC_4H_2O_4 \cdot 4H_2O$	...	0.88	...	...	...
Copper fumarate .....	$CuC_4H_2O_4 \cdot 2H_2O$	...	0.02	...	...	...
Copper maleate .....	$CuC_4H_2O_4 \cdot H_2O$	...	0.12	...	...	...
Lead fumarate .....	$PbC_4H_2O_4$	...	0.025	...	...	...
Lead i-malate .....	$PbC_4H_3O_4 \cdot \frac{1}{2}H_2O$	...	0.21	...	...	...
Lead maleate .....	$PbC_4H_2O_4$	...	0.052	...	...	...
Manganous fumarate	$MnC_4H_2O_4$	...	0.14	...	...	...
Nickel fumarate .....	$NiC_4H_2O_4 \cdot 5H_2O$	...	0.36	...	...	...
Silver fumarate .....	$AgC_4H_2O_4$	...	0.013	...	...	...
Silver maleate .....	$AgC_4H_2O_4$	...	0.12	...	...	...
Sodium acid fumarate	$Na_2C_4H_3O_4$	6.87	...	10.74	18.15	30.2
Sodium fumarate .....	$Na_2C_4H_2O_4$	22.83	...	...	...	...
Sodium acid maleate	$Na_2C_4H_3O_4 \cdot 3H_2O$	6.73	...	12.81	31.3	288.0
Sodium maleate .....	$Na_2C_4H_2O_4 \cdot \frac{1}{2}H_2O$	96.06	...	...	...	...
Strontium fumarate	$SrC_4H_2O_4$	...	0.29	...	...	...
Zinc fumarate .....	$ZnC_4H_2O_4 \cdot 5H_2O$	...	1.96	...	...	...

## STREATFEILD MEMORIAL LECTURE.

The Streatfeild Memorial Lecture was delivered by Mr. E. M. Hawkins, F.I.C., at the Finsbury Technical College, on October 25. He dealt with various aspects of Analytical Chemistry.

After reference to the value of the training which he and his former fellow students had received at the college under Meldola, Streatfeild and Castell Evans, the lecturer emphasised the importance of a knowledge of Physics, Mathematics and Physical Chemistry to the present-day Analyst and Consultant. He advised the students to qualify as soon as possible after the college course for membership of the Institute of Chemistry, and emphasised the importance of the Finsbury course in primarily training men for the practice of Chemistry.

First among the qualifications required in the analyst the lecturer placed accuracy and reliability, to which should be added the ability to decide to what degree of accuracy his results attained. He should also have a due sense of his responsibility in carrying out his work, especially when extensive repetition gave to it an appearance of drudgery.

Secondly, there was the need for rapidity to be associated with accuracy, as few students realised the speed of manipulation which would be required of them when they obtained a post after leaving college.

Thirdly, it was of great importance that the students should cultivate the gift of expressing his results suitably in a report, for much good experimental work was marred by the inability of the chemist to write up his results in such a way that the bearing of the work could be properly appreciated by those who read the report. It was necessary that the chemist should not be easily moved from an opinion formed after careful consideration of results which were obtained by honest work and patient investigation.

In conclusion, the lecturer stated that of the three classes of men practising chemistry—works' chemists, public analysts, consultants—the first class would greatly outnumber the public analysts when trade revived, whilst consulting chemists would be men of wide experience and high attainments who would be called upon by manufacturers to solve their problems, and should be highly remunerated for such work.

PROCEEDINGS AND NOTICES OF  
SOCIETIES.

PHYSICAL SOCIETY OF LONDON.

A meeting was held on Friday, October 26, at the Imperial College of Science, South Kensington, S.W.

The following papers were read:—

*The Fine Structure of Some Sodium Salts of the Fatty Acids in Soap Curds*, by S. H. PIPER, D.S.O., B.Sc., and E. N. GRINDLEY, B.Sc.

*X-Ray Analysis of Solid Solutions*, by E. A. OWEN, M.A., D.Sc., and G. D. PRESTON, B.A.

*Cohesion*, by DR. H. CHATLEY.

Proceedings of the meeting held on June 22, Alexander Russell, M.A., D.Sc., in the chair:—

*The Excitation and Ionization Potentials of Gases and Vapours*, by PROF. F. HORTON, M.A., D.Sc., F.R.S., Holloway College, University of London.

The study of ionization potentials dates back to the discovery of the phenomenon of the ionization of gases by collision, but the theoretical importance of a knowledge of the least difference of potential through which an electron must fall in order to acquire sufficient energy to ionize a gaseous atom or molecule on collision with it has greatly increased since the propounding by Bohr of his theory of atomic structure. Bohr's theory predicted the possibility of an atom being excited to emit radiation by the impact of an electron having energy in excess of a definite minimum amount—an amount corresponding to an "excitation" potential less than that required for ionization. This prediction has been verified experimentally for a large number of different atoms, and the study of excitation and ionization potentials has yielded strong support for the fundamental assumptions of the theory.

The experimental methods of investigation may be divided into two classes:—

(1) Those depending on the detection of the loss of energy by the colliding electron.

(2) Those depending on the detection of the radiation or ionization resulting from the collisions.

An account was given of several investigations by each method, and the results obtained were briefly summarised. The case of helium was referred to in greater detail. Bohr's view of the structure of the

helium atom was described, and the way in which it leads to the prediction of a metastable state of this atom was indicated. Experimental results in support of this view were quoted.

Finally, the prediction of the absorption by a normal atom of radiation emitted by another similar atom during the transition from an excited to the normal condition was explained, and the experiments by means of which the prediction has been verified were described.

THE SOCIETY OF PUBLIC ANALYSTS  
AND OTHER ANALYTICAL CHEMISTS.

The next meeting of the Society will be held on Wednesday, November 7, at the Chemical Society's Rooms, Burlington House, Piccadilly, W., at 8 p.m. The following papers will be read:—

*A Quantitative Study of the Limitations of the Reaction between Ammonia and Sodium*, by DINSHAW RATTONJI NANJI and WILLIAM SIMPSON SHAW.

*The Gold-Beaters' Skin Test for Tannins*, by PIYLLIS H. PRICE, B.Sc.

*Determination of Nitrogen in Coal*, by W. DONOVAN, M.Sc.

*The Estimation of Lead in Water and Urine*, by J. C. THRESH, D.Sc., M.D., F.I.C.

THE INSTITUTION OF ELECTRICAL  
ENGINEERS.

ORDINARY MEETING, NOVEMBER 1.

*Industrial Research, with Special Reference to Electrical Engineering Development*, by W. WILSON, B.E., M.Sc., MEMBER.

During the past 40 years, radical changes in manufacturing conditions have rendered industrial research essential for the attainment of reasonable efficiency and progress.

Industrial research is divisible into two orders, the more general and the more particular, both being necessary for the production of a new article. The second is usually termed "Development," and is the special subject of this paper.

While British men of science and applied science have been pre-eminent for general research, little attention has been paid to

development. Hence few inventions have, within recent years, been brought to their conclusion in this country, as compared with the great amount of original scientific work which has been successfully accomplished.

The reasons for this were analysed, and the cause is traced to lack of the co-operation necessitated by modern manufacture. This want is filled by development departments.

The various functions of the latter were dealt with. Their outcome is the removal of all non-standard work and technical troubles from the shops and drawing offices, and the provision of original and matured designs of new and improved articles for manufacture.

The negligible value of ordinary sources of novel suggestions was discussed, and the qualifications of a development man are deduced. The question of staffing the department, and the educational qualifications which the staff should possess, are then treated.

Practical matters, including buildings and equipment, procedure in development, the recording and filing of results and data, and the indexing of literature and information were discussed.

A short summary was given of the principal industrial research organisations in Great Britain, with a brief discussion on co-ordination.

#### THE SOCIETY OF GLASS TECHNOLOGY.

The first meeting of the Society of Glass Technology for the session 1923-24 was held in Sheffield on October 17, the President, Prof. W. E. S. Turner, D.Sc., in the chair.

"Frank Wood" Medals were presented to Mr. A. H. Sheen, B.Sc.Tech., and Mr. F. Winks, B.Sc.Tech., by Sir W. H. Hadow, C.B.E., M.A., D.Mus. The design of the medals was the work of Mr. Percy Metcalfe, a former pupil of Prof. W. Rothenstein, Professor of Civic Art in the University of Sheffield. Prof. Rothenstein pointed out that it had been the custom during the last century, when new medals were struck, to go to France for them, but whenever an Englishman got his chance, he showed that he could do this work much better than anyone else. People would not realise that to have faith in their own contemporaries was one of the first duties of citizenship.

A paper, illustrated by lantern slides, entitled, *The Effect of Titania on the Properties of Glass*, by A. R. SHEEN, B.Sc.TECH., and PROF. W. E. S. TURNER, D.Sc., was given by Mr. Sheen. Much has recently been shown in the production of heat resisting glass. Manufacturers, especially of scientific glassware, were realising the necessity of making a glass which had a high thermal endurance, and which was also capable of resisting the attack of substances with which the glass came into contact, whether solid, liquid, or gaseous. Modern heat resisting glasses contained a high percentage of silica and also boric oxide in considerable amount, *e.g.*, the well known glass, Pyrex (which owed its high thermal endurance to its exceptionally low coefficient of expansion, 0.0000032), contained approximately 80 per cent. silica and 12 per cent. boric oxide. In the case of silica the difficulty was to obtain a sufficiently high melting temperature. Glasses containing boric oxide were very readily melted, but here the objection was the effect of the oxide on the durability of the glass. Recent research in the Department of Glass Technology of Sheffield University has shown that as the  $B_2O_3$  content of a glass was increased, the durability towards water and acid increased to a maximum, and then, as the  $B_2O_3$  content was further increased, the durability fell off rapidly. Boric oxide containing glasses (and of course glasses with high silica content), on account of their acidic nature, were readily attacked by alkalis. What information there was concerning the use of titania in the production of glass seemed to point to the fact that titania glasses were heat resisting, but no experimental data were given. It was with this consideration specially in mind that this piece of work was undertaken.

At the outset, preliminary tests were made to find out what mixture of silica, titania and soda would give glasses at the highest temperature obtained in glass melting practice, *e.g.*, temperature of 1,400° to 1,450° C. It was found impossible to obtain a glass from silica and titania alone at this temperature. Batches were then calculated out on the basis of the glass formula:

$6 SiO_2 \cdot x Na_2O \cdot y TiO_2$ , where  $x + y = 2$ , and it was found that the first six members of the series gave glasses quite readily, *i.e.*, glasses of the approximate molecular compositions:—

(1)  $6 \text{ SiO}_2$ ,  $1.9 \text{ Na}_2\text{O}$ ;  $0.1 \text{ TiO}_2$ .

(2)  $6 \text{ SiO}_2$ ,  $1.8 \text{ Na}_2\text{O}$ ,  $0.2 \text{ TiO}_2$ ,  
etc. etc. etc.

(6)  $6 \text{ SiO}_2$ ,  $1.4 \text{ Na}_2\text{O}$ ,  $0.6 \text{ TiO}_2$ .

in which the soda was gradually replaced by titania. Above 1.8 mol.  $\text{TiO}_2$ , i.e., 13 per cent.  $\text{TiO}_2$ , it was found increasingly difficult to melt the glass, and higher temperatures were required.

It was found that if these glasses were melted under reducing conditions, their colour varied from light amber to dark brown. Therefore, part of the soda content was added as nitrate, and the melting operation was carried out in crucibles with well-fitting lids. By this means, colourless glasses were obtained.

There were indications during these melting operations that titania glasses were heat resisting. It was found in many cases that the glass could be removed straight from the furnace and allowed to cool down in the open air without splintering or cracking of the mass of glass occurring.

After considering the analyses of these six glasses, the first question dealt with was the durability of the titania glasses towards water. It was found on comparing with the corresponding lime and magnesia glasses that the titania glasses were less attacked than the lime glasses, especially in the earlier members of the series. The durabilities of the titania glasses were found to be practically the same as those of the corresponding magnesia glasses.

The annealing temperatures were found to be rather less than those of the corresponding lime and magnesia glasses.

Next, the important question of thermal expansion was dealt with. It was originally intended to determine this optically by the Fizeau-Pulfrich method, but after discussion it was eventually decided to repeat the melts on a large scale to draw tubing and determine the expansion by the ordinary dilatometer method. The thermal expansions of these titania glasses (only the first four glasses of the series were tested) were only slightly less than those of the corresponding lime glasses. Therefore, if titania glasses are heat resisting, it is certainly not due to their having a low expansion, as is the case with Pyrex glass, for example, but the cause must be sought in some other factor, such as tensile strength or elasticity.

These glasses possessed good working properties, their viscosity increasing as titania replaced soda. Throughout all the glasses melted in connection with this work there was hardly any evidence of devitrifica-

tion occurring. This bore out the statement of previous workers that titania hindered devitrification.

MR. A. COUSEN, B.Sc., A.R.C.S., then gave a paper entitled *The Estimation of Selenium in Glass*. - Illustrating his remarks with experiments, Mr. Cousen said that during researches on the use of selenium as a decolourising agent, it was found desirable to obtain a process for the estimation of selenium in the glasses obtained. The amount of selenium actually added to the batch was, in general, of an order sufficient to give only 1 part of the element per 42,000 parts of glass, or 0.0024 per cent., if no less occurred. Since, however, selenium was volatile at the temperature of the furnace (the boiling point at 1 atmosphere pressure is  $680^\circ$ ), values considerably less than the above were likely to be found. The only chemical method for estimating selenium in glass so far published was that of Fränkel, and described by Witt (Sprechsaal, 1914), and this was not quite comparable, since it dealt with proportions of selenium at least ten times as great as those it was desired to estimate.

The following modification of the above process was found to give results of fair accuracy. Twenty grams of finely powdered glass were dissolved slowly in hydrofluoric acid, and after standing in the cold, with the exception of selenium, the products of decomposition were dissolved by pouring into excess of boiling water. The selenium itself was filtered off on a filter pulp pad in a Gooch crucible. From the pad the selenium was removed by treating with a dilute chlorine solution (about one three-hundredth normal). To the filtered solution was added 1 cc. of 5 per cent. gum arabic and 5 cc. of half per cent. phenyl hydrazine hydrochloride—the whole being made up to 50 cc. Colloidal selenium was obtained, a yellow colour slowly developing, which was after half an hour matched against a standard solution of sodium selenite similarly treated. The method on testing with synthetic mixtures, gave results well within 0.0002 per cent. of the actual values, and a commercial glass, for which selenium had been used sufficient to give theoretically 0.0025 per cent., was found to contain actually only 0.0006 per cent. of the element.

To the discussion that followed there contributed the President, Messrs. W. J. Rees, J. H. Davidson, and J. R. Clarke. Mr. Cousen replied.

During the forenoon a party of members of the Society had an opportunity of visiting the River Don Works, Sheffield, of Messrs. Vickers, Ltd.

The next meeting will be held in the lecture room of the Coal, Gas and Fuel Industrial Department, the University, Leeds, on the afternoon of Wednesday, November 21.

### THE INSTITUTION OF ELECTRICAL ENGINEERS.

There will be a wireless section meeting in the lecture theatre of the Institution, on Wednesday, November 7. An inaugural address will be delivered by the Chairman, Mr. E. H. Shaughnessy, O.B.E.

### INSTITUTE OF METALS.

#### LECTURE ON AMERICAN METALLURGY.

Dr. W. Rosenhain, F.R.S., is to lecture before the Institute of Metals, London Local Section, on *Some Impressions of American Non-Ferrous Metallurgy*, on Thursday, November 8.

### THE INSTITUTE OF PHYSICS.

At the last meeting of the Board the following Corporate Members were elected:—*Fellows*: G. R. Bolsover, J. A. Jones, C. H. Lander, T. Takamine, A. Warren; *Associates*: K. R. Brain, A. L. Gregson, J. S. Grew, J. A. Hughes, E. O. Hereus, T. J. Lonsdale, R. D. Thompson, J. F. Wood.

### GENERAL NOTES.

#### NETHERLANDS.

##### TENDERS INVITED FOR VARIOUS GOODS.

Mr. R. V. Laming, O.B.E., the Commercial Secretary at The Hague, informs the Department of Overseas Trade that the Colonial Establishment, Westerdoksdijk 2, Amsterdam, is calling for tenders for various goods, tenders to reach the Director of the Colonial Establishment (through the Dutch representatives of United Kingdom firms) by 1 p.m. on October 31, 1923.

The goods required include white writing

paper, cardboard, packing, copying and miscellaneous paper, leather hat bands, hard haberdashery for uniforms, nails, shoe rivets and hooks and eyelets, ironmongery, zinc sheets, earthenware pipes, street cobbles, fireproof stone, bookbinders' glue, sealing wax, certain chemicals and oils, and soap and soap powder.

The tenders are called for under the usual general conditions, but the Department of Overseas Trade has available for inspection, by interested British firms, copies of the specifications (in Dutch), containing special requirements and dates of delivery. These may be seen on application to the Department at 35, Old Queen Street, S.W.1 (Room 84).

It will be noted that tenders must be submitted through local representatives. The Department will be pleased to place U.K. firms desirous of tendering and not represented in Holland, in touch with firms having branches in Holland who may be willing to act on their behalf in this matter. (Reference: 20890/F.W./G.P.).

### UNIFORMS AND GENERAL STORES FOR EGYPTIAN POSTAL ADMINISTRATION.

Mr. E. Homan Mulock, H.M. Commercial Agent for Egypt, reports that the Postal Administration at Alexandria is inviting tenders, to be presented in Alexandria by noon on November 15, 1923, for the supply of uniforms and general stores (including mail-bags, boots, calcium carbide, candles, furniture, hardware, lamps, steel stamps, etc.).

Further particulars may be obtained by interested United Kingdom firms on application to the Department of Overseas Trade, where a copy of the specifications, conditions, and form of tender, etc., is available for inspection up to October 31. After that date these documents will be forwarded on loan, in order of application, to firms in the provinces, who may be unable to arrange for their inspection by a London representative.

The Ministry of Agriculture and Fisheries has re-issued Leaflet No. 80, on *The Use of Artificial Manures*. It is pointed out that there are two main classes of manures:—

(1) Natural (organic)—the direct product of animals or plants, such as farmyard manure, seaweed, green manure, fish guano, &c.

(2) Artificial (inorganic)—this term is used quite correctly of such manures as superphosphate, nitrate of lime and others which are produced by processes of manufacture; it is also used, not quite correctly, of mineral manures such as mineral phosphate, potash salts and nitrate of soda, which are, strictly speaking, natural.

There are three forms of food which plants mainly require from the soil, nitrogen, potash and phosphates. Artificial manures, as a rule, supply only one of these forms. Each class—nitrogenous, potassic and phosphatic—comprises several kinds of manures which differ in their action. Thus in the nitrogen class, nitrate of soda is quicker in its action than sulphate of ammonia, and in the phosphate class superphosphate is quicker than raw phosphate. Or one kind may be more suitable to a certain crop than another, as, in the potash class, sulphate of potash is better than kainit for potatoes, and in the phosphate class basic slag is usually better for grassland.

Guidance is given as to the average quantities required by different crops. Three points require to be noted:

1.—If a plant is stunted in one of its requirements, even though other requirements are abundantly provided, the result will be little better than if it had been equally stunted of all.

2.—It is equally wasteful to use too much as too little manure. The right amounts will lie somewhere in the neighbourhood of what is here given; the actually correct amounts can only be learned by experience and by trial.

3.—Costs, both one's own and those given in records of trials, must be studied. The dressing which produces the highest yield is not always the most economical.

Of hardly less importance than the selection of manures is their distribution. Whatever amount of manure is employed, care should be taken to spread it equally over the soil. Artificial manures are easier to spread evenly when they are fine and free from lumps. It may be necessary to pass the material through a quarter-inch riddle, breaking all the lumps that fail to go through. Some manures change into hard lumps if stored for some months. This is one reason why it is seldom desirable to store manures for a long period. If this

has to be done, the addition of a small proportion of peat-litter dust or sawdust will help to keep them from caking. One often sees artificial manure being sown containing lumps as large as peas, and sometimes as large as walnuts. Not only does the presence of lumps prevent much of the crop getting its air share of the dressing, but the spots on which the lumps fall are actually poisoned, so that the plants are weakened or killed outright.

Where possible, manures, especially the slower acting manures, should be thoroughly mixed with the soil. For instance, where artificials are being applied to a corn crop, they should be applied at seed time, so as to get the benefit of the subsequent harrowing.

#### NOTICES OF BOOKS.

*Practical Physical Chemistry*, by ALEXANDER FINDLAY, M.A., D.Sc. Pp. XVI. + 298. Fourth Edition. London: Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 1923. 7s. 6d. net.

The first edition of Prof. Findlay's indispensable *Practical Physical Chemistry* appeared in 1906, and the third in 1914. Since the latter date the demand for the book has been met by the printing of new impressions.

Nearly a decade has elapsed since the subject matter has been revised, and hence, in the latest edition, he includes many alterations and extensive additions, yet the general character of the book as a student's laboratory companion remains unaltered.

New matter has been introduced, dealing with Cottrell's Ebullioscopic Method for determining Molecular Weights, and accounts of the Abbe Refractometer and Hilger's (constant deviation) Wave-length Spectrometer are also included.

Another important addition is a chapter containing a very suitable set of experiments illustrating some of the more striking properties of the colloidal state of matter.

It is now generally recognised that practical physical chemistry must form a part of a general chemistry curriculum, and the appearance of the present new edition should enable Prof. Findlay's volume to retain its popularity among both students and lecturers.

*Kelly's Directory of the Chemical Industries.* Pp. XXXI. + 903. 1923. Kelly's Directories, Ltd., 186, Strand, W.C.2. 30s.

Information is given concerning chemical manufacturers, manufacturing chemists, wholesale druggists, drysalts, chemists and drug stores (wholesale and retail). Full lists of the trades comprised will be found in this book.

The sections of Kelly's Directory of the Chemical Industries, 1923, include:—An alphabetical arrangement of the names in the towns and villages under each county, with the populations; a general classification of trades for London and its suburbs, i.e., classified lists of profession and trades with the names arranged alphabetically of those engaged therein; a similar classification for the rest of England, Scotland and Wales; the names for the principal towns of Ireland, arranged under towns and trades; and the names of the Channel Islands and the Isle of Man arranged under towns.

Another feature is the list of proprietary brands and articles which gives the makers' name and address after the name of the articles.

It is very apparent that many alterations have been necessary, and it need hardly be pointed out that out-of-date directories are often the cause of much inconvenience and irritation. This applies to those for the chemical industries as well as others.

*Report of the Oxygen Research Committee.* Pp. VII. + 177; with 43 text figs. and 6 plates. 8s. 6d. net. By post 8s. 9d. Published by H.M. Stationery Office for the Dept. of Scientific and Industrial Research.

This report describes certain aspects of the work of the Oxygen Research Committee since its appointment in 1919. It deals chiefly with the technical difficulties which have hitherto restricted the commercial utilisation of liquid oxygen and liquid air, and describes in particular recent improvements in the methods of handling the liquefied gases on a practical commercial scale. The work of the Committee has been carried out principally in the Heriot Watt College, Edinburgh, and the Air Ministry Oxygen Laboratory.

The subject matter of the report is arranged under the following headings:—

Part I.—*The Storage of Liquefied Gases:* The vacuum vessel; the physics of the vacuum vessel; experimental analysis of heat entry; adsorbents and adsorption.

Part II.—*The Manufacture of Metal Vacuum Vessels for Liquefied Gases:* Defects of containers and vaporisers; improvements in the design of vaporiser receptacles; the assembly of vacuum vessels; the testing of vacuum vessels; the problem of evacuation; evacuating plant.

Part III.—*Vacuum Vessels in Use:* Glass vacuum flasks; the transference of liquefied gases; some results of the periodic testing of vaporisers; decay of vacua in metal flasks.

Part IV.—*The Transport of Liquefied Gases and Compressed Gases:* Protection and support of containers in transit; losses during transport; railway regulations for the transport of liquid air; the transport of compressed oxygen.

Appendix.—Physical Data.

Index.

Copies may be obtained through any bookseller, or direct from H.M. Stationery Office.

#### BOOKS RECEIVED.

*Van Nostrand's Chemical Annual*, by JOHN C. OLSEN, A.M., PH.D. Pp. XXII. + 900. Fifth issue, 1923. Messrs. Constable & Co., Ltd., 10-12, Orange Street, W.C.2. 21s. net.

*Smith's General Chemistry for Colleges*, by JAMES KENDALL. Pp. XIII. + 747. 1923. Messrs. Bell, York House, Portugal Street, W.C.2. 18s. 6d. net.

*Recent Developments in Atomic Theory*, by LEO GRAETZ, Professor of Physics in the University of Munich. Pp. XI. + 174. 1923. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C.2. 9s. net.

*Chemical Engineering Catalog*, by THE CHEMICAL CATALOG COMPANY, INC. Pp. 1,050. Eighth Annual Edition, 1923. The Chemical Catalog Company, Inc., 19, East 24th Street, New York, U.S.A.

*The Manufacture of Nitric Acid and Nitrates*, by ALLIN COTTRELL, M.Sc., F.I.C., M.I.CHEM.E. Pp. XV. + 554. 1923. Messrs. Gurney & Jackson, 33, Paternoster Row, E.C.4. 36s. net.

*Elementary Chemical Calculations*, by MARTIN MEYER, Ph.D., College of the City of New York. Pp. VI. + 131. 1923. Oxford Book Company, 175, Fifth Avenue, New York, U.S.A.

### PUBLICATIONS RECEIVED.

Bulletins issued by the U.S. Department of the Interior, Bureau of Mines:—

*The Electrothermic Metallurgy of Zinc*, by B. M. O'HARA. Pp. VI. + 106.

*Timbering of Metal Mines*, by E. A. HOLBROOK, RICHARD V. AGETON, and HARRY E. TUFFT. Pp. VII. + 72.

*Water-Gas Tar Emulsions*, by W. W. ODELL. Pp. IV. + 51.

*Leaching Nonsulphide Copper Ores with Sulphur Dioxide*, by CHARLES E. VAN BARNEVELD and EDMUND S. LEAVER. Pp. V. + 91.



This list is specially compiled for *The Chemical News*, by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

25111—British Cellulose & Chemical Manufacturing Co., Ltd.—Treatment of cellulose derivatives. Oct. 9.

25328—Crundall, S. F. W.—Production of titanium compounds. Oct. 11.

25274—Thorn, I.—Process of hardening products of condensation from phenols and aldehydes. Oct. 10.

25478—Hoffman la Roche & Co., Akt.-Ges. F.—Manufacture of emulsions of bismuth salts. Oct. 12.

#### Specifications Published this Week.

182803—Ges. Fur Kohlentechnik.—Process and apparatus for separating ammonia and benzol hydrocarbons from coal distillation gases.

187592—Howard, H.—Process for the production of hydrogen sulphide.

192703—Soc. d'Etudes Chimiques pour l'Industrie. Process for the manufacture of urea from cyanamide.

#### Abstract Published this Week.

202743—Hypodermic injections.—Kato, J., of 33, Ekandocho, Kamikyo-ky, Kyoto, Japan.

*Hypodermic injections; colloidal sols.*—A remedy to be injected into hæmorrhoids consists of a colloidal suspension of metallic magnesium in a harmless and chemically inert liquid such as glycerine, olive oil, or liquid paraffin. The colloidal suspension is prepared by finely powdering the magnesium, suspending it in the glycerine, &c., and passing an electric current of 2 amps at 40 volts between platinum electrodes for a period of two hours with continuous stirring and cooling. The preparation is stored in an atmosphere of hydrogen or nitrogen.

*Lignone sulphonic acids; pulp, preparation of.*—Wood and like lignified materials are resolved by treatment at 100-110° C. with a strong aqueous solution of sulphurous acid which is originally substantially free from sulphuric acid. Preferably the process is carried out in a digester lined with acid-resisting cement, and the materials under treatment are rapidly agitated. In an example, wood prepared as for the bisulphite process is treated with six times its weight of a seven per cent. solution of sulphurous acid purified from sulphuric acid. The mass is heated with open steam for six hours; then steam at a temperature of 105-110° C. is employed for a further ten hours to complete the resolution. The liquor containing the lignone derivatives may be evaporated to dryness, preferably under reduced pressure, or prepared in concentrated form for transport. These derivatives are stated to be different from those contained in sulphite-cellulose liquor.

*Sulphurous acid* for use in the process is rendered free from sulphuric acid by treatment with barium sulphite or, according to one Provisional Specification, with barium acetate or bisulphite.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

#### JOURNALS FOR SALE.

JOURNAL OF THE CHEMICAL SOCIETY, 1915, 1920, complete with Indexes, £1 each year. Journal of Industrial & Engineering Chemistry, 1919, £1. *Chemical News*, 1921, 1922, 15s. each year. All unbound, but in excellent condition.—H.E., c/o *The Chemical News*, 97, Shce Lane, London, E.C.4.



# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3317.

## BRITAIN HER OWN CHEMIST.

### PROGRESS OF A VITAL INDUSTRY.

A sum of £100,000 is to be spent on the Chemical Section of the British Empire Exhibition at Wembley next year. It is to occupy 40,000 square feet in the Palace of Industry, and it will be built in such a way as to form a self-contained hall within the Palace. It is intended to present to the public a complete picture of the present state of the British Chemical Industry. No important firm in the industry will be unrepresented, and their exhibits will number over a hundred.

In an interview last week, Mr. W. J. U. Woolcock, C.B.E., General Manager of the British Association of Chemical Manufacturers, said that the chemical hall, in which the exhibits will be grouped, would be the most comprehensive exhibition of the products of British science and industry ever brought together. It would certainly be the biggest thing British chemical industry has yet attempted, and there will be every hope of impressing the Empire both with their present position and their prospects.

They were not going to be content with an impressive spectacle of past achievements; they desired to illustrate what is behind the processes of production. They hope, also, to show that by reason of British invention and research there are guarantees that the industry will never be left behind again.

A group of the best scientific minds in this country are co-operating with the Association in illustrating the advances made in the last 20 years in every branch of pure chemical science. The importance of the chemical industry in the daily life of any nation is vital, and they are going to illustrate it. There is the sulphuric acid industry, which is such an index of national prosperity that Disraeli once said: "The measure of a country's prosperity can be gauged by the amount of sulphuric acid it

is producing per head of population." The alkali industry is one of the most important of the chemical industries, too, and its development is one of the romances of Britain.

Then there are all those industries which have arisen out of the distribution of coal, the production of coal-tar products, and the preparation of the thousand and one substances of the dyestuff and fine chemical industries. The discovery of the first artificial colouring matter was made in England; its development was, as one might expect, left to the Germans. In 1913, 80 per cent. of the dyestuffs used in this country were obtained from Germany and Switzerland; to-day we produce 80 per cent. of what we require, and import only 20 per cent.

The discoveries of British chemists in the class of chemicals called antiseptics have been instrumental in saving thousands of valuable lives, and such discoveries are only the beginning. The extraordinary progress made in recent years in British laboratories has helped to make the disease-ridden lands within and without the Empire safe for the white man. Without these remedies, some of which are quite new to science and have been elaborated during and since the war, British colonization and trade in the tropics and sub-tropics would be seriously handicapped.

Chemistry is the "open Sesame" of modern industry. The constant scientific control of the manufacture of foodstuffs, of the means of locomotion, of the supply of gas and water, is essential in modern life. The establishment of a complete British chemical industry is a great achievement. The Association considers it vital that the Chemical Section at the British Empire Exhibition should adequately represent the growing importance of the industry. That is why the Committee is taking such pains to ensure that the display they are arranging shall be fully represented.

We certainly think that whatever damage the war may have done to the industry, good support and representation in the matter will again put it on a substantial and even more progressive basis. J.M.

—(By courtesy of the British Empire Exhibition, 1924, Inc.)

## ARE THE NATURAL GROUPINGS OF THE ELEMENTS AND THE SPECTRAL LINES OF HYDROGEN RELATED?

### PART III.

By F. H. LORING.

In continuation of the above subject—see *The Chemical News*, 1923, Vol. CXXVII., pp. 273-275—the question arises as to whether the argument presented can be strengthened by taking into consideration certain phenomena that may be in some unknown way related thereto.

Since the atom is now believed to be a planetary system in which the electron represents the planet and the nucleus of the

atom the sun, a consideration of our solar system in connection with these studies is of interest. It is possible that a planetary system such as our solar system is not an ideal one to compare with the so-called planetary system of hydrogen. Sir O. Lodge has practically raised this question, but so far as the writer is aware, no direct or indirect relations have been found comparable in exactitude with Bode's Law. It will be seen from the accompanying table that the groups  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$  afford direct values which, so far as they extend, agree about as well with certain planetary distances as do Bode's figures, especially when the comparison is made in the manner indicated in the table referred to.

#### SEMI-MAJOR AXIS OF ORBIT.

	Bode's Law.	Earth=10.	Diffs.	Millions of Miles / 10.	Groups.	Diffs.
Mercury	0 + 4 = 4	3.87	+0.13	3.6	—	—
Venus	3 + 4 = 7	7.23	-0.23	6.72	7	+0.28
Earth	6 + 4 = 10	10.00	0.00	9.29	9	-0.29
Mars	12 + 4 = 16	15.23	+0.77	14.16	13	-1.16
Asteroids	24 + 4 = 28	27*		25†	21	
Jupiter	48 + 4 = 52	52.02	-0.02	48.33	48	-0.33
Saturn	96 + 4 = 100	95.39	+4.61	88.62	—	—
Uranus	192 + 4 = 196	191.90	+4.1	178.28	—	—
Neptune	384 + 4 = 388	300.70	+88	279.35	—	—

\* This is a mean value, the extremes being below 25.5 to above 28.5.

† This is a mean value, the extremes being below 23.7 to above 26.5.

Above planetary data taken from Kaye and Laby's "Tables of Phys. and Chem. Constants."

#### NOTES.

In the column giving the distances from the sun in millions of miles divided by 10, it should be noted that the figures are mean ones.

With regard to the asteroids, or minor planets as they are often termed, there may have been a planet of moderate size and of small mass, between Mars and Jupiter, which was reduced to comparatively small fragments by disruption. There are over 800 minor planets, the largest having a diameter of about 400 miles.

It has been shown mathematically that if such a catastrophe had occurred, the orbits of the small bodies should at some time in their paths pass through the place where the disruption took place in space, but this coincidence is apparently not the case. From other considerations, such as a series of catastrophes, the calculation may require revision, so that the whole problem of the asteroids is one that should not necessarily carry weight in the argu-

ment against the rules made evident in the above table.

It is to be noted that the smallest mean distance for the minor planet Medusa is 198,134,000 miles; so that in a remote sense the group forms a kind of mass band (their planes do not coincide), one edge of which corresponds fairly closely with the value 21.

The following quoted paragraph from the first of a series of articles on the atom by Sir O. Lodge, in *Beama*, of July, August, September, October, 1923 (continued), is of interest, but the agreement between Bode's law and Bohr's law of orbital radii in respect of the hydrogen atom is not as close as are the  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$  group values in the comparison given above in the table. Lodge says:—"The electric case is simpler than the planetary, for the planets differ in mass as well as in distance, whereas the electrons are all alike and differ only in distance from the centre. Every orbit will have its characteristic moment of momentum, and if we could say that this moment of momentum, having a certain value 1 for an

innermost orbit, was 2 for the next, 3 for the next, and so on, it would be delightfully simple. In other words, if the moment of momentum, or what is practically the same thing, the rate of sweeping areas, is not only constant for each orbit, but proceeds by equal steps or simple multiples from one orbit to the next, how much simpler the law of succession would be than the at present unknown law of succession of the planets—the discovery of which was attempted long ago by the astronomer Bode. Well, strange to say, *this simple law does appear to hold rather accurately for the atomic orbits.* This was discovered not by Bode, but by Bohr. Calling the unit moment of momentum a *lot* (which is a convenient name employed by auctioneers for an indivisible group which you can take or leave as a whole), the moments of momenta characteristic of successive orbits have to be 1 lot, 2 lots, 3 lots, etc., as the orbits increase in radii; and the result is that the radii of successive orbits proceed as the squares of the natural numbers, provided the law of attraction is as the inverse square of the distance—as for electrical attraction we know it is. Because, according to Kepler's Third Law,  $r^3$  varies as  $T^2$  (cube of distance proportional to square of periodic time), or, what is the same thing, the product  $rv^2$  is the same for all the orbits. Hence  $vr$  proceeds according to the natural numbers, 1, 2, 3, 4, etc., in arithmetical progression, the radii  $r$  must proceed according to the squares of these numbers, 1, 4, 9, 16, etc. This is algebraically necessary. These are the successive Bohr orbits, which seem to be the only stable and permanent ones; no other orbits seem possible. A particle [electron] may drop from one orbit to the next, but it cannot rest or revolve in any intermediate position. The full reason of this has still to be discovered, but the fact is evidenced by many considerations."

An interesting view in connection with Bode's law is discussed by Miss M. A. Blagg in a paper in the *Royal Astronomical Society Monthly Notes*, 1913, vol. 73, p. 414.

Referring to the diagram shown on page 258, this is reproduced to the scale of about  $\frac{1}{2}$  millimeter per unit, but the values were re-proportioned to bring them into the range of the plotting selected. In the case of the wave lengths, the original unit was increased by dividing them by 30. The

group values were raised by multiplying them by 3.

The calculation, quite apart from the plotting, is obviously a simple one, viz.:—Wave length ( $\lambda$ ) in Angstrom units minus 3540, divided by 61.5 = the group values; that is to say,  $(\lambda - 3540)/61.5 = \alpha, \beta, \gamma, \&c.$

The figures given on page 274 of Part II. as being representative of the fine lines of hydrogen in respect of the H $\alpha$  line resolution, were taken from Foote and Mohler's book, "The Origin of Spectra," 1922; but the noughts before the decimal places should be cancelled.

*Corrections.*—On page 258, right-hand column, fifth line down, "first" should read "prior." On page 274, left-hand column, fourth line from bottom, "since" should read "moreover." On same page, right-hand column, second line from top, "and by" should read "which." Further down, paragraph beginning with "Apart," first line, "these" should read "the." The large table of figures, etc., should be labelled at the top "SCHEME." On page 275, right-hand column, second line from top, "when considering" should read "as compared with."

## RECENT RESEARCHES IN ORGANIC CHEMISTRY.

By R. F. HUNTER, F.C.S.

(Continued from page 263.)

In July, 1921, a short paper by Fairbourne and Toms on a Monosodium glyceroxide, in which preparations of a Monosodium Glyceroxide,  $\text{CH}_2(\text{OH})\text{CH}(\text{OH})\text{CH}_2\text{ONa}$ , Glycerol 2:4 Dinitro phenyl ether,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OCH}_2(\text{OH})\text{CH}_2\text{OH}$  2:4 Dinitro phenyl allyl ether, 2:4 Dinitro Hexyl Dibromopropyl ether,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\text{OCH}_2\text{CHBrCH}_2\text{Br}$ , were described.

The third part of Burton and Trinner's investigations on influence of nitro groups on reactivity of substituents in benzene nucleus, partial reduction of dinitro toluenes by  $\text{SnCl}_2$  and  $\text{HCl}$ , in which the action of ammonia on 3:4 dinitro oxylene was also studied, appeared. The fourth part, communicated at the same time, dealt with the condensation of ethyl 3 and 5 nitro 2 chlorobenzoates with hydrazines, had Kenner and Witheim as its authors, and the experimental part gave an account of the action of hydrazine hydrate on ethyl 2 chloro 5 nitro benzoate and derivatives. 4 nitro 2 carbethoxy phenyl hydrazine,

$\text{NO}_2 \text{C}_6\text{H}_5(\text{CO}_2\text{Et}) \text{N H N H}_2$ , benzaldehyde  
4 nitro 2 carbethoxy phenyl hydrazone, 5  
nitro 3 keto 1 : 3 dehydroindazole,



5 amino 3 keto 1 : 3 dehydroindazole were  
examined.

The action of phenylhydrazine on ethyl 2  
chloro 5 nitro benzoate was studied, and  
compounds 5 nitro 3 keto 2 phenyl 1 : 3 de-  
hydroindazole, 3 chloro 5 nitro indazole, 3  
chloro 5 nitro 2 phenylindazole, 7 nitro 3  
keto 1 : 3 dehydroindazole prepared.

The action of the same reagent on ethyl  
2 chloro 3 nitro benzoate was examined  
with the preparation of 2 nitro 6 carbethoxy  
hydrazobenzene,

$\text{NO}_2\text{C}_6\text{H}_3(\text{CO}_2\text{Et}) \text{N H N H C}_6\text{H}_5$ ,  
and of 7 nitro 3 keto 2 phenyl 1 : 3 dehy-  
droindazole.

In July, Morgan and Webster's paper on  
the isomeric diazonium salts of dehydro-  
thio toluidine appeared. They found these  
to exist in syn and anti modifications and  
prepared.

1 Phenyl 5 methyl benzothiazole 4' azo  
naphthol syn and anti 1 phenyl diazohydro-  
chlorides, Potassium syn and anti 1 phenyl  
5 methyl benzothiazine,

4' diazo oxides,

Sodium syn and anti phenyl 5 methyl  
benzothiazole,

4' diazosulphonates,

Syn and anti 1 phenyl 5 methyl benzo-  
thiazole,

4' diazo cyanides,

4' Cyano 1 phenyl 5 methyl benzothia-  
zole,

Syn 1 phenyl 5 methyl benzothiazole 4'  
diazo salts, such as acid diazo chromate,  
nitro prusside, ferricyanide, diazo carbon-  
ate, diazo chlorate, and diazo ortho borate.

A paper was published by Mason on  $\beta$   
Hydroxy  $\beta$  3 : 4 methylenedioxy phenyl  
ethylamine and derivatives at this time.

$\beta$  Hydroxy  $\beta$  3 : 4 methylenedioxy  
phenyl ethylamine and its salts and deriva-  
tives were prepared.

Part II. of Perkin and Titley's work on  
Epi-camphor appeared also at this time,  
and among the substances prepared and  
examined were:

Hydroxy methylene 1 epicamphor,

Benzoyloxy methylene epicamphor,

Hydroxy methylene epicamphor semi  
carbazone,

Anilinomethylene epicamphor,

$\beta$  Naphthyl aminomethylene epicamphor,

Aminomethylene epicamphor,  
l and d epicampholenonitrite,  
l and d epicampholenic acid,  
Dihydroepicampholenolactone, and  
dl campholenic acid.

Published at the same time was the first  
part of King's work on derivatives of sul-  
phur in commercial salvarsan and the ex-  
perimental part contains an account of  
reduction of 3 nitro 4 hydroxy phenyl-  
arsenic acid with sodium hyposulphite, iso-  
lation of 3 amino 4 hydroxy 5 sulphino-  
phenylarsenic acid and 3 : 3' Diamino 4 :  
4' dihydroxy 5 : 5' disulphino arsenoben-  
zene.

Oxidation of 3 amino 4 hydroxy 5 sul-  
phino phenylarsenic acid to 3 amino 4 hy-  
droxy 5 sulphophenylarsenic acid 3 : 3' di-  
amino 4 : 4' dihydroxy 5 : 5' disulphino-  
arsenobenzene.

3 : 3' Diamino 4 : 4' dihydroxy 5 sul-  
phino arsinobenzene hydrochloride.

3 : 3' Diamino 4 : 4' dehydroxy 5 sul-  
pho 5' sulphino arsenobenzene.

The action of magnesium phenyl haloids  
on diphenyl chloroacetyl chloride, and the  
constitution of triphenylvinylalcohol was  
studied by McKenzie and Boyle, who ex-  
amined the constitution of the alcohol, the  
actions of Mg Ph Br and Mg Ph I on di-  
phenylchloroacetyl chloride, and that of Ph  
Mg Br on triphenylvinyl alcohol.

Some new tri cyclic bases by Moore and  
Doubleday appeared at the same time,  
among which mention may be made of the  
following:—1 : 4 endo methylene 6 methyl  
tetra hydro quinoxaline and 1 : 4 endo  
ethylene 6 methyl tetra hydro quinoxaline  
and 1 : 4 endo tri methylene 6 methyl  
tetra hydroquinoxaline.

Three other papers also appeared by  
Atack which dealt with the structural iso-  
merism of oximes, criticism of the Hantzsch  
Werner hypothesis, and a new theory of  
constitution of isomeric oximes. The  
author summarised his results in the fol-  
lowing way:—

(1) The Hantzsch Werner hypothesis of  
the stereo isomerism of oximes is criticised  
in view of the fact that it fails to explain  
characteristic reactions of the so-called syn  
and anti oximes, their mode of interconver-  
sion, etc., and further, fails to interpret  
Beckmann reaction as applied to the ben-  
zildioximes.

(2) A new structural theory of isomerism  
of oximes is advanced, which explains satis-  
factorily the number of isomerides known  
to exist, the differences in the salt forming

properties of the oxime groups present in isomeric oximes and formation of O and N ethers.

The paper on the structural isomerism of oximes, Part II., was summarised thus:—

(1) A fourth isomeric benzildioxime, M P 217°, has been prepared, differentiated by colour and behaviour of nickel compound, and by other reactions from the three known benziloximes.

(2) The Hantzsch Werner hypothesis only admits of the existence of 3 isomeric benzildioximes, whereas the structural theory admits of six.

Hepworth and Clapham's paper on the action of Grignard reagents on organic sulphur compounds contained an account of the action of magnesium phenyl, ethyl bromide, and of magnesium benzyl chloride on benzene sulphonyl chloride. The action of magnesium methyl iodide on ethyl mercaptan and preparation of thio esters from magnesium ethyl thiol bromide.

The action on ethyl thiobenzoate of Mg Et Pr and Mg Ph Pr, and on di isoamyl sulphoxide, diphenyl sulphoxide phenyl benzyl sulphoxide and trimethylene trisulphoxide.

Action of Mg Me I on diphenylsulphone, phenyl benzylsulphone, trimethylonetrissulphone and ethyl phenylsulphoneacetate.

Watson and Dult's paper, from Bengal, on dyes derived from phenanthraquinone contained preparation of azine derivatives of phenanthrene, 2 amino phenanthra-phenazine,

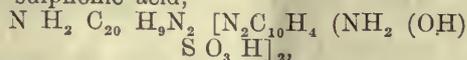


- 4 Aminophenanthraphenazine,  
 2 : 7 Diaminophenanthraphenazine,  
 4 : 5 Diaminophenanthraphenazine,  
 2 : 7 Diaminodihydrophenanthraphenazine,  
 2 : 7 Dihydroxy dihydro phenanthraphenazine,  
 2 : 7 : 11 Triaminophenanthraphenazine,  
 2 : 7 Diamino 15 hydroxy phenanthra-naphthazine 13 sulphonic acid,  
 2 : 7 Dinitro 15 hydroxy phenanthra-naphthazine 13 sulphonic acid,  
 2 : 7 Dinitro 11 : 4' dimethyl flavinduline chloride,

Phenanthraquinone 2 : 7 bis (2') azo 7' amino hydroxynaphthalene 3' sulphonic acid,

$\text{C}_{14}\text{H}_6 \text{ O}_2 [\text{N}_2 \text{ C}_{10} \text{ H}_4 (\text{NH}_2) (\text{OH}) \text{ S O}_3 \text{ H}]_2$ ,  
 Phenanthraquinone 4 : 5 bis (2') azo 7' amino 1' hydroxynaphthalene 3' sulphonic acid,

11 Aminophen anthra phenazine 2 : 1 bis (2') azo 7' amine 1' hydroxy naphthalene 3' sulphonic acid,



and

2 : 7 Diaminophenanthraquinone di-phenyl hydrazone p p' disulphonic acid.

The second part of Naik's paper on dithio ketones and ethers was communicated in June to the T.C.S., and contained in the experimental portion references to the preparation of dithio mesoxo p toluidide, the o compound, dithio mesoxo  $\alpha$  and  $\beta$  naphthylamine,

Dithio mesoxomone p toluidide,

Dithio mesoxomonophenylamide,

Ethyl dithio mesoxo p tolylamide,

Ethyl dithio mesoxo o tolylamide,

Methyl malono p toluidide disulphide,

Methyl malono o toluidide disulphide,

Methyl malono  $\alpha$  toluidide disulphide,

Methyl malono dimethylamide disulphide.

The interaction of ethyl so-diocyanoacetate, ethyl sodiomalonate, ethyl cyanoacetate, and of ethyl malonate and  $\text{S}_2\text{Cl}_2$ , and also of 1 : 1 dimethyl cyclo hexane 3 : 5 dione and sulphur monochloride, 3 : 5 : 3' : 5' tetraketo 4 : 4' bis dithio 1 : 1 : 1' : 1' tetra methyl di cyclo hexyl 2 : 2' disulphide was carried out.

Interaction of cyclohexane spiro cyclohexane 3 : 5 dione and  $\text{S}_2\text{Cl}_2$ . 1 : 1' di cyclo hexanespiro 3 : 5 3' : 5' tetra keto 4 : 4' bis dithiodi cyclo hexyl 2 : 2' : 6 : 6' bis disulphide.

Interaction of cyclopentanespiro cyclohexane, 3 : 5 dione and  $\text{S}_2\text{Cl}_2$ , cyclopentane spiro 3 : 5 diketo 4 dithio cyclohexane gave a  $\gamma$  disulphidoacetone carboxydi-amine.

Ethyl  $\gamma$  phenylcarbamyl a  $\gamma$  bis disulphido acetate a  $\gamma$  disulphidoacetone dicarboxydi p toluidide.

Two papers by Hepworth are worthy of note. The first, on the action of Grignard reagent on trivalent organic iodo compounds, containing an account of the action of magnesium powder on iodobenzene dichloride and p iodo toluene dichloride. The second paper was on the accelerated formation of magnesium, alkyl and aryl haloids.

Dudley's paper, entitled *Amino acylcholine esters*, deserves mention, and contains an account of glycyclocholine platino and auri chlorides,  $\text{N Me}_3 \text{ Cl C}_2\text{H}_5 \text{ O CO CH}_2 \text{ NH}_2 \text{ H Cl Pt Cl}_4 \text{ H}_2\text{O}$ , and  $\text{N Me}_3 \text{ Cl C}_2\text{H}_5 \text{ O CO CH}_2 \text{ N H}_2 \text{ H Cl}_2 \text{ Au Cl}_3$ .

A paper on the action of sodium on phenylacetate was published by Perkin and described:

2 Methyl benzo  $\gamma$  pyrone, dehydroacetic acid,

1 Hydroxy 3 methylxanthone, its methyl ester, and 2 4 nitro 1 hydroxy 3 methylxanthone.

Mills, Harris and Lambourne's research on the Doebner-Miller quinaldine synthesis contained, among other things, the synthesis of 6 Ethyl quinaldine.

Coffey and Ward's paper on allyl compounds deserves mention, as does the former's paper on linoleic and hexabromostearic acids, published at the same time. At this time a further piece of Goddard's work appeared, and contained an account of thallium dimethyl and diethyl *o*, *m* and *p* nitro phenoxides, and also of dinitro and trinitro phenoxides.

Simonsen and Rems' synthesis of 1 : 6 di hydroxy 2 methyl anthraquinone appeared about this time, in the experimental part of which reference is made to 3 nitro 2 methoxy *p* toluic acid and 3 nitro 2 methoxy *p* toluidine.

Two papers which appeared at this time and deserving mention, are those on the cupri tartarate, by Packer and Wark, and the labile nature of halogen atoms in substituted nitro methanes, by Macbeth and Pratt, and the colorations produced by substituted nitro forms by Macbeth and Graham. Two papers also appeared by McBain and his co-workers on the hydration of the fibres of soap curd.

Two papers were also published by Perkin and Robinson and Perkin and Scarborough. The first on "Studies of Configuration of *aa'* Dibromodibasic Acids, Pt. I., The Dibromoadipic Acids and Synthesis and Resolution of trans cyclo pentane 1 : 2 : 3 tri carboxylic acid." The second on "Resolution of dl trans cyclo pentane 1 : 3 dicarboxylic acid," appeared in the T.C.S. for July.

Coffey's second paper on oxidation of drying oils appeared in the same issue, and contained  $\alpha$  and  $\beta$  Linolenic acids and linolic acid.

The second part of King's work on Salvarsan contained the study of the Monosulphonation of *p* nitro phenol, the diamination of 6 nitro 4 amino phenol *o* sulphonic acid, 6 nitro phenol *o* sulphonic acid, and an account of 6 amino phenol *o* sulphonic acid and its nitration and the reduction of isomeric nitro amino compounds to the same 4 : 6 diamino phenol *o* sulphonic acid.

Krishna's paper on Phenolcoumarin and

Resorcinolcoumarin deserves mention, published at the same time as Cohen and Froelicher's research on the nitro and amino derivatives of *m* hydroxy benzoic acid. This paper contains an account of 4 amino *m* hydroxy benzoic acid and its derivatives.

Hamer's paper on isomeric iso cyanines contains details of the preparations of quinaldine and quinoline derivatives and methiodides, such as nitro, amino, quinaldines, cinnamylamine, quinaldine, and quinolines.

Short's method for preparation of acyl phenyl hydrazines appeared at this time with Burrow's and Turner's paper on additive compounds from arsines which describes compounds such as Ph Me<sub>2</sub> As, P I<sub>3</sub> and Ph Me<sub>2</sub> As, As I<sub>3</sub>.

They also published an account of the alkylation of nitroprussic acid.

Kenner and Witham's paper on the influence of steric factors on intra molecular condensation was communicated in August, 1921, to the Chemical Society, and contains the preparation of 7 chloro 1 hydrindone and 5 chloro 1 hydrindone.

Henstock's paper on 9 : 10 dehydrophenanthrene is worthy of note.

The third part of McLeod and Robinson's researches on pseudo bases, dialkyl aminomethyl alkyl ethers, and sulphides, was also published at this time, and is of some interest. An interesting and characteristic property of pseudo basic carbinols is the formation of ethers by simple treatment with alcohols.

Further work on terpenes, by Henderson and Marsh, has appeared in the form of the study of action of hypochlorous acid on pinene and the preparation of pinene dichlorohydrins, C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>Cl<sub>2</sub>, and of chlorohydrins, C<sub>10</sub>H<sub>17</sub>O<sub>2</sub>Cl.

Two papers by Heilbron and Buck were published together, on the reactivity of double conjugated unsaturated ketones, the first on 4' dimethylamino 2 hydroxy distyryl ketone, and contains a description of the compound and various analogous and ketonic bodies, such as OH C<sub>6</sub>H<sub>4</sub>CH : CH CO CH : CH C<sub>6</sub>H<sub>4</sub>N Me<sub>2</sub>C<sub>6</sub>H<sub>4</sub> (N Me<sub>2</sub>) CHO.

The additive compounds of 4' dimethylamino 2 hydroxy distyryl ketone, 4' dimethylamino 2 methoxy distyryl ketone were also examined.

The second paper deals with the action of hydroxylamine semicarbazide and phenylhydrazine on 4' dimethylamino 2 hydroxy distyryl ketone and its methyl ester, in the experimental part of which we find a description of the compound, O H C<sub>6</sub>H<sub>4</sub>HCH : CH

CO CH : CH C<sub>6</sub>H<sub>4</sub>N Me<sub>2</sub>N H<sub>2</sub>OH, and other analogous bodies.

Papers by Morgan and Challenor and Morgan and Burgess, on the ortho chloro dinitro toluenes, and referring to bases from 2 chloro 4 : 5 dinitro toluene and non-aromatic diazonium salts, have appeared, in which the condensation of 6 chloro 3 : 4 tolylene diamine with diketones and ortho quinones was studied, and the interaction of 6 chloro 3 : 4 tolylenediamine and formaldehyde (a) in neutral solution, (b) in acid solution.

The diazo reaction in the iso-oxazole series was also investigated, and compounds such as 3 : 5 dimethyl iso oxazole 4 azo acetyl acetone examined.

The paper by Fairbourne on ortho dimethyl anthraquinone and derivatives is of interest. Among the compounds prepared were 2 : 3 and 1 : 2 dimethylantraquinone and 1 : 2 dicarboxylic acid.

A long research on Harmine and Harmaline, the synthesis of norharman, by Kermack, Perkin and Robinson, has also appeared. It may be pointed out that the fused pyridine-pyrrole nucleus type of organic compound has received little, if any, attention. Harmine is methyl methoxy 4 carboline. The compounds norharmine and harman are obtained by elimination of the methyl and methoxy groups from harmine. The relation between harman and tryptophan was discussed in the *Journal of the Chemical Society*, 1919. The experimental work included the following preparations: Harman from tryptophan, harmolic acid, norharmol, norharman, 3 carboxyindole 3 acetic acid, etc. It also included the condensation of indole 2 carboxylic chloride with alanine ester and sodium derivative of ethyl acetoacetate, and a description of 6 methoxy indole, 11 methoxy 5 keto 4 : 5 dehydroindole diazine, and the synthesis of norharman and the study of 6 methoxy 3 methyl indole 2 carboxylic acid and of 6 methoxy 3 methyl indole.

The paper by Simonson on the essential oil from *andropogon waraneusa* and the constitution of piperitone is worthy of note.

A very interesting paper by Moir has appeared on the calculation of colour in cyclic substances, and a method of calculating the colour of dicyclic substances and monocyclic substances is detailed in the papers.

In October, two more papers were communicated by Morgan and Glover and Morgan and Vining. The first on the familiar subject of ortho chlorodinitro toluenes, dealt with 2 chloro 3 : 4 dinitro toluene. The

second paper was on dinaphtha 1:7:1':7' diquinone, and described the oxidation of dihydroxy naphthalenes with metallic peroxides. Compounds such as dinaphtha 1:7:1':7' diquinonetetra 2:4 dinitro phenylhydrazone, the reduction of dinaphtha 1:7:1':7' diquinone, by H. I. Henry, and Paget's paper on chenopodium oil also appeared at this time.

Fargher and Perkin's paper on *m* opianic acid is of interest, and contains references to homoveratrole, ketonic derivatives, the oxidation of 4:5 dimethoxy *o* tolyl methyl ketone, 4:5 dimethoxy phthalonic acid, the action of aniline on 4:5 dimethoxy phthalonic acid, *m* opianic acid (4:5 dimethoxy *o* aldehydo benzoic acid) and its derivatives.

In September, Read and Andrews' paper on studies of halogenohydrins and related derivatives of cinnamic acid, Part I., was communicated. Among the questions studied were: The addition of H·Cl·O and of H·Br·O to cinnamic acid and to methyl coumaric acid.

The application of Hofmann's reaction to substituted phthalimides, by Moore, Marack and Proud, appeared at the same time.

Smiles and Stewarts' paper on *m* dithiobenzoic acid appeared at this time.

Copisarow's paper on Freidel Crafts Reaction, migration of alkyl groups in benzene nucleus, deserves a mention. Smiles and McClelland's research on the derivatives of 3 oxy-(1)-thio naphthene is of interest, and contains in the experimental part details of the interaction of ethyl acetoacetate and 2 thiolbenzoic acid, and the isolation of condensation products and derivatives.

Shimomura and Cohen's new method for resolution of asymmetric compounds was published at the same time, and contains a description of the preparations of 1 menthyl dl phenyl chloroacetate, C<sub>6</sub>H<sub>5</sub> CH Cl·CO<sub>2</sub>·C<sub>10</sub>H<sub>19</sub>, 1 menthyl dl phenylbromoacetate, C<sub>6</sub>H<sub>5</sub> CH Br CO<sub>2</sub>·C<sub>10</sub>H<sub>19</sub>, 1 menthyl dl bromophenylpropionate, C<sub>6</sub>H<sub>5</sub> CH<sub>2</sub> CH Br·CO<sub>2</sub>·C<sub>10</sub>H<sub>19</sub>.

The action of SO Cl<sub>2</sub> on 1 menthyl dl mandelate and that of P Cl<sub>5</sub> on bromopropionyl bornylamide and other analogous substituted amido-bodies was also studied.

In Perkin and Plant's research on derivatives of tetra hydrocarbazole, the reduction products of carbazole are of interest because of their relations to strychnine.

Tetra hydrocarbazole and 9 methyl tetra hydro carbazole were oxidised to 9 methyl carbazole.

Bennet and Whincop's paper on deriva-

tives of monothio ethylene glycol appeared in September, and contained descriptions of a number of new and complex aliphatic sulphur compounds, such as  $\beta\beta'$  di p nitro benzoyloxydiethyl disulphide, ethylene bis  $\beta$  hydroxy ethyl sulphide, ethylene bis  $\beta$  chloroethyl sulphide, sulphido bis  $\beta$  hydroxydiethyl sulphide, and 2:4 dinitro phenyl  $\beta$  hydroxy ethyl sulphide,  $C_6H_3(NO_2)_2 S \cdot CH_2 CH_2 OH$ .

Crompton and Triffitt's short paper on Dichloroacetates and Chlorobromoacetates from a  $\beta$  Dichlorovinyl ethyl ether is worthy of note.

In October, Morgan and Hickenbottom's paper on Studies in n Butyl Series, Part I., Aryl and n Propyl ketones, appeared, and the extensive experimental part contained much that was important in connection with these comparatively simple bodies.

Grant and Pyman's research on the Nitro- and Amino-derivatives of 4 Phenylglyoxaline appeared at the same time, in which 2 Thiol 4 phenylglyoxaline and 4 phenylglyoxaline were described. The nitration of 4 phenylglyoxaline led to the isolation of 4o and 4p nitro phenylglyoxalines. The nitration of 4p nitro phenylglyoxaline gave 5 nitro 4 p nitro phenyl glyoxaline.

The benzoylation of 4 phenylglyoxaline and its nitro derivatives was also accomplished.

Towards the end of August, Ray published a paper on synthesis in the Thianthren series. The method of condensation employed was to dissolve the substance in dry  $CS_2$  in a flask filled with the acid of a reflux condenser and dropping funnel, and containing  $S_2Cl_2$ . The catalyst (aluminium foil) was inserted previous to addition of  $S_2Cl_2$ . The following were studied: Dichloro thianthren, dichlorodimethylthianthren, diacetyl amino thianthren, dimethoxy thianthren, diacetyl thianthren, dibenzyl thianthren, thianthren dicarboxylic acid.

Singh and Lal's studies on Aryl derivatives of bis iminocamphor are worthy of mention. They prepared oo' di tolylenebis imino camphor, oo' dimethoxy diphenylene bis imino camphor, pp' diphenylene bis imino camphor, and pp' bis iminocamphor diphenylamine.

Duff's paper on cis phthalate, cis homo phthalate, and other ethylene diamine cobaltic salts is of note. Among the compounds studied were: cis phthalatediethylene diamine cobaltic salts, cis o sulphobenzoate diethylene diamine cobaltic salts, cis bromobenzene 3:4 disulphonate diethylene diamine cobaltic salts, cis homophthalate

diethylene diamine cobaltic salts, trans dichlorodiethylene diamine cobaltic hydrogen benzyl sulphoacetate, and trans dichloro diethylenediamine cobaltic hydrogen sulphobenzoate.

Rowe and Levin's researches in the dihydronaphthalene series, the ar dihydro a naphthols and derivatives, were published about this time.

In December, 1921, there appeared Silberad's researches on Sulphuryl Chloride, Part I., Influence of catalysts. Among the catalysts employed were: iodine, thionyl chloride, sulphur, sulphur chloride, ferric chloride,  $AlCl_3$ , and mixed catalysts.

Cohen and Crabtree's paper on Structure and Colour of Azine Scarlets appeared at this time, and was summarised by themselves in this way:—

1.—The formation of quaternary methochloride has only slight effect on the tint of the parent hydrochloride.

2.—Transition from a simple amino group through a mono-alkylated to a dialkylated amino group is accompanied by gradation in tint from pure scarlet, through scarlet magenta to pure magenta.

3. Transference of both amino groups to same nucleus produces a fundamental change in colour.

4.—Replacement of benzene by naphthalene or tetra hydroquinoline nucleus produces little change on tint.

5.—Absence of radicles in nucleus enhances the blueness of shade.

Among their work were preparations of: 3 amino 7 dimethylamino 2 methyl phenazine metho chloride; 3 amino 7 dimethylamino 2:8 dimethylphenazine metho chloride; 5 aminonaphtha phenazine 7 metho chloride 9 amino; 5 dimethylamino 10 methyl naphthaphenazine hydrochloride; 9 amino 5 dimethylamino 10 methyl naphtha phenazine metho chloride; 3 amino 7 dimethylamino phenazine metho chloride; 3:7 tetra methyl diaminophenazine; 3 amino 2 methyl N methyl tetra hydro quinolinophenazine metho chloride; 3 amino 7 methylamino 2 methyl phenazine metho chloride; 3 amino 7 methylamino 2:8 dimethyl phenazine metho chloride; 3 amino 7 benzylamino 2:8 dimethyl phenazine metho chloride; 3:7 diamina 2:8 dimethyl phenazine metho chloride; 3:7 diamino 8 methyl phenazine metho chloride; and 5:9 diamino 10 methyl naphtha phenazine metho chloride.

Fairbourne and Toms' new synthesis of osazines appeared in December, and contained in the experimental part 2:4 dinitro



phenyl hydroxy ethyl ether, and 6 amino 2:3 dihydro 1:4 benzisoxazine.

Dult, Whitehead and Wormall's paper on the action of diazo salts on aromatic sulphon amides, Part I., appeared at the same time, and contained a description of the action of benzenediazonium chloride on *p* toluene-sulphoamide.

The action of *o* toluenediazonium chloride on the same, and of *m* toluene diazonium chloride on the same.

The action of *p* toluenediazonium chloride and *p* chlorobenzenediazonium chloride on *p* toluene sulphoamide.

The action of benzenediazonium chloride, *o* toluenediazonium chloride, *m* and *p* toluenediazonium chlorides on benzenesulphoamide, and lastly of *p* chlorobenzenediazonium chloride on benzenesulphoamide.

Mills' and Nodder's paper on optically active forms of keto dilactone of benzophenone 2:4:2:4' tetracarboxylic acid deserves mention.

The last paper published in 1921 was by Ruth King, on the production of picric acid from sulphonic acids of phenol. The work contained the examination of 6 nitro phenol 2:4 disulphonic acid and nitrolysis of sulpho groups in the ortho and para positions.

#### DR. MULLER'S X-RAY SPECTROGRAPH.

To meet the requirements of various classes of users, including crystallographers, chemists, metallurgists, radiologists, and others, Dr. Müller has designed, and Messrs. Adam Hilger, Ltd., 75a, Camden Road, London, N.W.1, have placed on the market at the price of £44, an extremely compact form of X-ray Spectrograph. While of sufficient accuracy, the instrument is made of simple design and at such cost that it can be put into the hands of advanced students who are capable of profiting by experience of this important class of work.

The instrument consists of a support carrying a rotating table for the crystal mount, and passing through the latter a bar of triangular section upon which slide carriers for slit and plate-holders respectively. This support is mounted on a box containing a spring-motor, to the shaft of which is attached a cam. A lever, which can be clamped at any orientation to the axis of the crystal table, is kept in contact with the

cam by a spring, and is thus oscillated through a certain angle as the cam rotates. With the cam usually supplied an angle of oscillation of about 12° is obtained.

The crystal mount consists of a vertical plate with lead screen, to which the crystal can be attached with soft adhesive wax and which is provided with tilting adjustment about a horizontal axis. The mount can be traversed in a slide across the rotating table so as to bring the face of the crystal up to the axis of rotation. The edge of the table is divided in degrees to facilitate the setting relative to the lever in order to register lines upon each side of the normal to the photographic plate.

The slit consists of two brass blocks 26 mms. long, which can be clamped at a known distance apart, one of a number of "feeler" gauges supplied being inserted between the jaws before clamping.

The plate-holder, which is attached to its slide by two milled head screws, is designed to take plates 12 cms. x 1.9 cm., which can be cut from standard size plates ( $\frac{1}{2}$ -plate size). It is provided with a black paper screen, so that the instrument may be used in daylight without risk of fogging the plate, and no special sheath for the plate is necessary.

In order to measure the distance between the centre of rotation and the surface of the photographic plate, a steel rule divided in millimetres is supplied, which will pass through the slit mount. The centre of rotation of the table is determined by a fiducial mark upon a pin which can be inserted in the table when the crystal mount is removed. This is quickly done by unscrewing the retaining screw of the spring top and sliding the mount out of its groove.

The instrument is mounted on three levelling screws, the heads of which, as well as those of other adjusting screws, are made of vulcanite to minimise risk of shock in case the instrument is charged by induction from the tube and transformer, etc. A lead screen is also mounted upon the instrument to prevent fogging of the plate by stray X-radiation.

The instrument is available for work with a single crystal by the Bragg method. By a simple interchange of parts which can be effected in about one minute, it becomes suitable for the investigation of powders by the Debye method. The slit jaws, crystal mount and plate-holder are removed, and the carriers moved up to support a circular camera, 6 cms. in diameter, which carries a

photographic film. The camera is so disposed that a powder-holder can be inserted in the centre of the rotating table and advantage taken of the oscillating movement for this work also. In place of the slit is mounted a brass block pierced with an aperture of 1 mm. in diameter. The end of this block fits into an aperture of the camera and points directly to the powder-holder in the centre.

The instrument is also available for taking photographs by Hull's powder method, a small spring, which can be quickly attached to the slit, being supplied. Thus the three standard methods now in use are available in the one instrument.

The motor is such as to give about 40 oscillations per hour to the crystal, and to run nearly 8 hours without rewinding.

### GENERAL NOTES.

#### MINERAL PRODUCTION OF CANADA, 1922.

The High Commissioner for Canada in London has received from the Dominion Bureau of Statistics at Ottawa the following finally revised statistics on the production of Non-Metallie Minerals in Canada during 1922.

With the exception of arsenic there were no outstanding differences between the production of 1922 and the previous year of the commodities listed in the table below as miscellaneous non-metallie minerals.

The production of arsenic in 1922 was 2,576 tons, an increase of 1,085 tons, or 42 per cent., when compared with 1921. Large quantities of this commodity are being used in the United States for insecticides which are found to be particularly effective in combating the boll weevil, an insect which has caused great damage in the cotton districts during recent years.

	1922.	
	Quantity.	Value in Dols.
Actinolite .....	Tons 50	575
Arsenic (white) produced from Canadian ores .....	" 2,576	321,037
Barytes .....	" 289	9,537
Chromite .....	" 767	11,503
Feldspar .....	" 27,727	248,402
Fluorspar .....	" 4,503	102,138
Graphite .....	" 597	31,353
Grindstones .....	" 1,005	43,742
Magnesite .....	" 2,849	76,294
Magnesium sulphate .....	" 1,021	24,017
Manganese .....	" 73	2,044
Mica .....	" 3,349	152,263
Mineral water .....	Gals. 221,443	14,220
Natro-Alunite .....	Tons 50	2,500
Iron oxides .....	" 7,285	110,608
Peat .....	" 3,000	14,500
Phosphate .....	" 190	1,796
Pyrites .....	" 18,143	74,303
Quartz .....	" 109,947	208,598
Sodium carbonate .....	" 202	3,027
Sodium sulphate .....	" 504	11,980
Talc .....	" 13,195	188,458
Tripolite .....	" 219	5,781
Total .....		1,658,676

### THE DESTRUCTION OF PLATINUM CRUCIBLES.

The destruction of platinum crucibles, which is always attributed to a chemical change in the platinum, can be prevented (according to a publication by Heraens), if unnecessarily high temperatures in heating the crucible are avoided. The combinations of platinum with carbon, silicon, boron, phosphoric acid, etc., arise through reduction of the salt being heated at relatively high temperatures. The ease with which hydrogen and hydro-carbons pass through glowing platinum makes such a reduction easy. The use of acetylene for heating platinum is, for this reason, especially dangerous. Melted alkalis, alkaline carbonates, in the presence of sulphur, or potassium cyanide, strongly attack platinum at high temperatures.

Easily fusible metals and easily reducible metallic oxides cannot be treated in platinum, and the same is true of all substances which give off chlorine, bromine, iodine, sulphur or phosphorus.—*Chemiker-Zeitung*, July 24, 1923.

### THE WORLD'S AGRICULTURAL RESULTS.

On the basis of statistical data and other information published in the October International Report of Agricultural and Commercial Statistics of the International Institute of Agriculture, Rome, the results of the Northern Hemisphere harvests are now ascertainable, together with estimates for some of the more important crops in the Southern Hemisphere.

The aggregates for the Northern Hemisphere (exclusive of Russia) in 1923 surpass those of 1922 by 7.6 million metric tons of wheat (10 per cent.), by 3.2 million of rye (15 per cent.), 2.8 million of barley (13 per cent.), 6.4 million of oats (14 per cent.). These increases mainly arise from plentiful yields in Europe and North Africa, where a favourable season was experienced, in sharp contrast with the drawbacks suffered last year by the grain crops. In North America and in Asiatic countries the totals are very similar to last year's, which showed good results.

A preliminary estimate, quite provisional, from the Southern Hemisphere is available from Argentina, where the wheat yield is forecasted at 6.8 million tons, which is the highest figure on record for that country,

and shows an increase of 1.6 million metric tons (31 per cent.) over last year. Again, in Australia, the area under wheat is nearly similar to that in 1922, and good yields are anticipated, as conditions are favourable during growth.

It may, therefore, be regarded as certain that the aggregate production of these four grain crops is considerably larger than it was last year. This is not all, for the recent crops of wheat and oats, with barley also in minor degree, are actually larger than those immediately before the war. Comparisons are available from the recently published International Yearbook of Agricultural Statistics issued by the Institute. Apart from Russia, the harvests of 1923, inclusive of all those countries which have supplied data, exceed the averages furnished in the Yearbook for 1909 to 1913 by 12.4 million metric tons of wheat (16 per cent.), 3.3 million of oats (7 per cent.), and 0.7 million metric tons of barley (3 per cent.). Rye alone falls short by 1.4 million (5 per cent.).

Taking the several continents separately the European and North African crops are nearly equal to those of the pre-war period, though none of the four attains a parity. The ascertained increases as compared with pre-war figures are therefore consequent on extensions in the other continents, particularly in America.

Available data for the Northern Hemisphere maize crops are not quite so complete, as data are not yet to hand from Rumania, Jugoslavia and a few other countries. An increased yield of 5.2 million metric tons (7 per cent.) may be already indicated, however, owing almost entirely to the plentiful crop in the United States.

As regards linseed, special reference is due to the exceptionally large yield in Argentina, where the preliminary estimates are for 1.9 million metric tons, or 0.8 million more than last year's yield, which was in itself a very good one. Taking into account the fine harvests of linseed in other countries whence data are to hand, the yield already tabulated amounts to 3.2 million metric tons, and indicates an increase of 55 per cent. over last year's yield.

The aggregate yield of sugar-beet in the countries which have already supplied data—which represents rather over 50 per cent. of the world's total yield—comes out decidedly larger than that corresponding of 1922: 21.1 million metric tons as compared with 19.2 million, or 10 per cent.

more. It would seem that the sugar content too is likely to be higher.

Potatoes, on the other hand, are expected to yield a much poorer aggregate than last year. The countries which have furnished data, representing slightly over one-half of the world's production (apart from Russia), report a yield of 65.5 million metric tons, as compared with 80.1 last year, showing a decrease of 18 per cent. When considering these results it should, however, be borne in mind that 1922 was a year of exceptional plenty for potatoes, the then yield being far above the average.

### AUSTRALIA'S OVERSEAS TRADE IN JULY.

The Officer in Charge for His Majesty's Senior Trade Commissioner in Australia has forwarded to the Department of Overseas Trade a brief resumé of the returns of the Commonwealth's overseas trade for the month of July.

These returns show, in comparison with the corresponding month last year, an increase in imports of nearly £2,000,000, while exports show a decrease of over £2,500,000. The value of imports exceeded exports by £6,500,000.

Imports of boots and shoes showed an increase as compared with the corresponding period in 1922, while cotton and linen, silk and woollen piece goods showed a decrease. Imports of petrol (£453,828) more than doubled, and chassis for motors (£679,659) increased by £266,439.

Exports of wool were over £2,200,000 in value below those of July, 1922. Shipments of gold exceeded those in the same period by £134,877. Exports of Australian products from the States were:—

	£
New South Wales .....	1,699,053
Victoria .....	989,732
Queensland .....	1,198,221
South Australia .....	687,443
Western Australia .....	784,696
Tasmania .....	22,178

The Northern Territory imported £930 worth of merchandise; there were no exports.

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### THE ROYAL SOCIETY.

THURSDAY, NOVEMBER 1.

Papers read:—

E. G. T. LIDDELL and SIR CHARLES SHERINGTON, PRES. R.S.: *A Comparison between certain Features of the Spinal Flexor Reflex and of the Decerebrate Extensor Reflex respectively.*

J. BARCROFT, F.R.S., and H. BARCROFT: *The Blood Pigment of Arenicola.*

The blood pigment of *Arenicola Marina* differs from the hæmoglobin of human blood in certain respects.

(1) The  $\alpha$  band of the oxy-hæmoglobin is situated 18 Angstrom units nearer the violet, and

(2) The  $\alpha$  band of the CO-hæmoglobin is situated 11 A.U. nearer the violet than the corresponding human band.

(3) The dissociation curves show a greater affinity for both oxygen and carbon monoxide than those of human blood under similar conditions.

(4) The affinity for CO is about 70 times that for oxygen, as compared with 250 in man and 140 in the mouse. The possibility of a relationship between the position of the bands and the affinity of the pigment for gas is discussed.

(5) The main unloading of oxygen from the pigment of *Arenicola* would appear to be between 1 and 3 mm. pressure.

(6) The mean oxygen capacity of the hæmoglobin per gram of *Arenicola* is about 0.01—0.013 cc.

A comparison between the oxygen capacity of the pigment and the total oxygen consumption of the worm reveals the fact that the pigment holds sufficient oxygen to supply the animal for 1-2 hours, and probably acts as a reserve to tide it over the period at low-water when its hole is closed.

T. DEIGHTON: *The Basal Metabolism of a Growing Pig.* Communicated by Prof. T. B. Wood, F.R.S.

Various alterations in the calorimeter described in *J. Agric. Sci.*, vol. 11 (1921), are mentioned, and certain modifications of technique described.

The basal metabolism of a pig has been measured at various ages from 75 days up-

wards, and it has been shown that in the pig, as in human beings, the metabolism per unit area is greater in mid-youth than at any other time of life.

Experiments are adduced to show that the metabolism after the ingestion of food reaches a maximum after 5 hours and then declines.

The curve of basal metabolism showing its variation with age is discussed, and reasons are given for thinking that this increase of metabolism in youth is directly ascribable to growth.

The rationing of pigs for maintenance and growth is discussed, and it is concluded from the experimental results achieved that the curve of rationing for growth and maintenance, without fattening, cannot possibly be a two-thirds power curve

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#### ROYAL INSTITUTION OF GREAT BRITAIN.

The General Monthly Meeting was held on November 5.

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#### THE ROYAL SOCIETY OF ARTS.

On Wednesday, November 7, the inaugural address of the 170th session, entitled *Exhibitions*, was delivered by LORD ASKWITH, K.C.B., K.C., D.C.L., Chairman of the Council, and a Vice-President of the Society.

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#### THE INSTITUTION OF MINING ENGINEERS.

##### ANNUAL GENERAL MEETING—PRELIMINARY NOTICE.

The thirty-fourth annual general meeting will be held at the rooms of the Geological Society, Burlington House, Piccadilly, London, W.1, on Thursday, November 29, 1923. An agenda-programme will be sent to members in due course.

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#### MINERALOGICAL SOCIETY.

ANNIVERSARY MEETING, TUESDAY,  
NOVEMBER 6, AT 5.30.

The following papers were read:—

DR. L. J. SPENCER: *Euclase and Platinum from Diamond Washings in British Guiana.*

H. E. BUCKLEY: *The Anomalous Optical Properties of Freshly Prepared Mixed Crystals of Seignette Salt.*

COL. N. T. BELAIEV: *On the Genesis of Widmanstätten Structure in Meteorites and Terrestrial Alloys.*

PROF. L. R. WILBERFORCE: *Illustration and Detection of Inclined and Horizontal Dispersion in Bi-Axial Crystals.*

A. RUSSELL: *On the occurrence of the Rare Mineral Nadorite in Cornwall, and of Beraunite (Eleonorite) in Co. Cork, Ireland.*

A. F. HALLIMOND and F. R. ENNOS: *On Moravite from North Wales.*

DR. G. T. PRIOR: *On the Chemical Composition of the Ashdon Meteorite.*

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#### THE CHEMICAL SOCIETY.

##### VAN DER WAALS MEMORIAL LECTURE.

This was delivered by DR. J. H. JEANS, Sec. R.S., at the Institution of Mechanical Engineers, Storey's Gate, Westminster, S.W.1, on Thursday, November 8, 1923, at 8 p.m.

The following papers were read at the Ordinary Meeting, Nov. 1:—

*The Rapid Admixture of Hot Combustible Gases with Air*, by F. M. CRAY and W. E. GARNER.

The minimum temperature at which hot combustible gases will ignite, when mixed with air at high speeds, must be higher than the normal ignition temperature. It should be possible to demonstrate the cooling effect of the air if sufficiently high speeds of projection of the hot gases be attained.

Experiments were carried out in which high explosives in steel containers, and acetylene and oxygen mixtures in glass bulbs, were exploded in a limited volume of air. The ignition of high explosives is to some extent determined by the volume of air into which the hot gases are projected, ignition occurring only when the ratio of

weight of explosive to volume of air exceeds a definite value.

In the experiments with acetylene and oxygen, the velocities of projection were not sufficiently high for this. Partial ignition occurred whatever the ratio of explosive mixture to the surrounding air, but ignition was less complete the higher the velocity of projection. Thus the greatest conversion of acetylene to carbon monoxide was attained with mixtures of equal proportions of acetylene and oxygen, this mixture, as was shown by Dixon, possessing the highest velocity of explosion of any acetylene-oxygen mixture.

Although carbon monoxide was present in the products from the explosion of all of the mixtures investigated, free carbon was found only in those experiments where the ratio of oxygen to acetylene exceeded unity. This behaviour is in agreement with the views of Bone on the mechanism of the processes occurring during the combustion of hydrocarbons.

*The determination of Surface Tension from the maximum pressure in Bubbles. Part II.,* by SAMUEL SUGDEN.

An improved form of apparatus for measuring surface tension by the method of maximum bubble pressure was described. The method of calculation has been simplified.

*The variation of Surface Tension with Temperature, and some related Functions,* by SAMUEL SUGDEN.

The variation of surface tension with temperature is known to be represented with fair accuracy by an equation of van der Waals (1894),

$$\gamma = K_1 \theta_c V_c - \frac{2}{3}(1-m)$$

in which B is a universal constant. On the other hand, Ferguson (1916) allowed this exponent to vary slightly in order better to express the data of Ramsay and Shields (1893). Recently it has assumed a new interest, since Ferguson has shown that the simple relation, discovered by Macleod (1923), between surface tension and density can be deduced from the modified Ramsay-Shields law and the equation, if B is constant (1.20).

The data of Ramsay and Shields are now known to be in error owing to their correction for capillary rise in the outer vessel having been inadequate. The author now calculates the necessary correction by applying an earlier (1921) theory.

From the available figures it was shown, for six non-associated liquids, that:—

(a) The variation of surface tension with temperature can be represented accurately by:

$$\gamma = \gamma_0(1-m)^{1.20},$$

where  $\gamma_0$  is a constant and m is the reduced temperature:

(b) Macleod's relation,

$$\gamma = C(D-d)^4,$$

where C is a constant and D, d are the densities of liquid and vapour respectively, holds with remarkable accuracy up to within a few degrees of the critical temperature;

(c) Van der Waals' relations connecting  $\gamma_0$  with the critical constants are only approximately true.

*Muconic and hydromuconic Acids. Part III.: Valency interchange in the Hydromuconic system,* by E. H. FARMER.

It was shown in Part I. that the products of interaction of sodiomalonic and sodiocyanoacetic esters with ethyl muconate possessed the general structure  $RO_2C \cdot CH_2 \cdot CH_2 \cdot CX \cdot CH \cdot CO_2R$  and not  $RO_2C \cdot CH \cdot CH \cdot CHX \cdot CH_2 \cdot CO_2R$ . This constituted an addition of a 1:3-type; and in view of the difficulty in accounting for such a movement of the double bond as is necessitated if 1:2-addition be supposed to take place, it was suggested that the muconic system was to some extent comparable in mobility with the glutaconic system.

This view is now seen to be incorrect. The muconic system is static, conforms to stereo-chemical theory, and adds the components of esters at the 1:2-position. The substituted dihydromuconic esters thus produced represent in their configuration interesting instances of the effect of an equilibrium between  $\Delta\alpha$ - and  $\Delta\beta$ -dihydromuconic esters in the presence of sodium alkoxide. This equilibrium, which favours the  $\Delta\alpha$ -form in the esters themselves, results in the conversion of the additive products under consideration into  $\beta$ -substituted glutaconic esters.

*Experiments on the Synthesis of Substances possessing the Ladenburg Formula. Part I.: Derivatives of cyclopropylcyclopropane,* by E. H. FARMER.

Recent syntheses by Beesley and Thorpe suggested a method for the syntheses of substances possessing the Ladenburg formula. The production of considerable quantities of various derivatives of cyclopropylcyclopropane was described.

## CORRESPONDENCE.

To the Editors of THE CHEMICAL NEWS.

SIRS,—Could any of your readers inform me what is the lowest pressure at which the Joule Thomson Effect is produced on passing air through a small orifice at ordinary temperatures?

The lowering of temperature may be exceedingly small, and I am desirous of knowing what is the initial pressure which will produce the slightest cooling effect at ordinary room temperature. I do not want to produce a very low temperature, only down to 0° C. by continually cooling the incoming gas.—Yours, &c.,

A. J. FURLAND.

Swansea, November 1, 1923.

## ELECTRODE REACTIONS AND EQUILIBRIA.

A general discussion on this subject will be held by the Faraday Society, meeting at the Institution of Electrical Engineers, on Monday, November 26 next. The first session of the meeting will extend from 3 to 5 p.m., and will deal with "Conditions of Equilibrium at Reversible Electrodes." Sir Robert Robertson, President, will preside, and the introductory address will be given by Dr. E. K. Rideal. Among the speakers will be Professor Billman, of Copenhagen, who will read a paper on "Some Oxidation and Reduction Electrodes and their importance to Organic Chemistry." After an interval for tea, the meeting will resume at 5.30 p.m., and will devote itself to the consideration of "Irreversible Electrode Effects, including Passivity and Over-voltage." Prof. F. G. Donnan, Vice-President, will preside over this session, and the introductory address will be given by Professor A. J. Allmand. At the conclusion of the meeting a dinner will be held at the Holborn Restaurant, to be followed by an informal conference. Members of the Chemical Society, the Physical Society, and the Institution of Electrical Engineers have been invited to attend this discussion. Others interested should apply to the Secretary of the Faraday Society, 10, Essex Street, London, W.C.2. from whom a full programme may be obtained.

## PUBLICATIONS RECEIVED.

The Colour Users' Association have issued a little brochure for 1923-4 containing useful general and special information, including lists of members, dyestuff statistics, regulations, tables, and other data, which it is a convenience to have at hand.

## BULLETINS ISSUED BY THE DEPARTMENT OF THE INTERIOR, UNITED STATES GEOLOGICAL SURVEY.

*Bismuth, Selenium, and Tellurium*, by VICTOR C. HEIKES. Pp. 16 to 24.

*Lead in 1922*, by C. E. SIEBENTHAL and A. STOLL. Pp. 27 to 36.

*Zinc in 1922*, by C. E. SIEBENTHAL and A. STOLL. Pp. 37 to 52.

*Lead and Zinc Pigments and Salts in 1922*, by C. E. SIEBENTHAL and A. STOLL. Pp. 77 to 85.

*Asphalt and Related Bitumens in 1922*, by K. W. COTTRELL. Pp. 7 to 13.

*The Lime Belt of Massachusetts and Parts of Eastern New York and Western Connecticut*, by T. NELSON DALE. Pp. VI. + 71.

*Progress Report on a Sub-surface Study of the Pershing Oil and Gas Field, Osage County, Oklahoma*, by W. W. RUBEY. Pp. 1 to 70.

*Surface Water Supply of the United States 1919-1920. Part I.: North Atlantic Slope Drainage Basins*, by NATHAN C. GROVER.

*Surface Water Supply of the United States, 1919-1920. Part X.: The Great Basin*, by NATHAN C. GROVER. Pp. VI. + 348.

*Surface Water Supply of the United States, 1919 and 1920. Part XII.: North Pacific Slope Drainage Basins*, by NATHAN C. GROVER. Pp. V. + 262.

Messrs. Theodor Steinkopff, of Dresden, have just published a volume on *Physical Chemistry as Applied to Internal Medicine*, by Prof. H. Shade, Director of the physico-chemical division of the Clinic at Kiel.

The development of physical chemistry has assisted in the progress of many sciences in recent years. That it has helped in medicine is well borne out by a perusal of this work.



This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 26037—Lantz, R.—Manufacture of naphthaquinone derivatives. Oct. 18.  
 26163—Oechslin, C.—Manufacture of substituted products of an aliphatic arsenic acid. Oct. products of an aliphatic arsenic acid. Oct. 19.  
 25665—Pereira, H.—Manufacture of perylene vat dye. Oct. 15.  
 25666—Pereira, H.—Manufacture of 3-10-perylene quinone. Oct. 15.  
 25936—Soc. l'Oxyhydrique Francaise.—Manufacture of hydrogen. Oct. 17.

#### Specifications Published this Week.

- 184462—Moeller, Dr. F.—Waterproofing cellulose or carbohydrates of the cellulose group.  
 199401—Pereira, H.—Reduction of dioxyperylene.  
 203347—Lilienfeld, Dr. L.—Manufacture of cellulose derivatives.

#### Abstract Published this Week.

- 203077—Synthetic drugs.—Pomaret, M., of 92, Rue Vielle du Temple, Paris, and May & Baker, Ltd., Garden Wharf, Church Road, Battersea, London.

*Arsenobenzene derivatives.*—Stable solutions of 3 : 3 -diamino-4 : 4 -dihydroxyarsenobenzene and like arseno bases with reducing sugars are prepared by acting with an organic base, for example piperazine, upon a neutral soluble condensation product of the arseno base having one or more side chains directly linked to a nitrogen atom, and then adding a solution of a reducing sugar; or the reaction may be effected in the presence of a sugar. In an example 3 : 3 -diamino-4 : 4 -dihydroxyarsenobenzene-N-methylene sulphonylate dissolved in glucose solution is treated with piperazine; the solution is ready for use after standing for a few days. Specifications 112,984 and 117,283 are referred to. The Provisional Specification also mentions hexamethylenetetramine as a suitable organic base.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

## NOTICES.

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# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3318.

## CHEMISTRY AT THE BRITISH EMPIRE EXHIBITION (1924).

At the British Empire Exhibition at Wembley the national life of this country and of the newer nations overseas will reveal itself in every branch of its activities. In every art, craft and manufacture, and in agriculture, we hope to make a memorable display.

Clearly, therefore, we cannot neglect to make an exhibition of our progress and present position in science, more particularly in chemical science which is imperceptible to most, but nevertheless clearly intertwined with our progress and position in industry, with the preservation of our health and with our enjoyment of such amenities as our civilisation has as yet provided.

We are so familiar with the idea that we are behind other nations in chemistry, particularly behind Germany. I am not talking about the application of chemistry, but the study of chemistry and of research in chemistry at our universities, that the thought may arise, is it wise to make such an exhibit? Would it not be better, as chemistry is so fundamental, as our progress in industry depends so much upon our progress in pure chemistry, to conceal our position in this science—at least for a time—from the prying gaze of the world that will visit Wembley? The answer to that is this:—

The pure chemistry exhibit is being organised by a committee composed of representatives of the Association of British Chemical Manufacturers, of the Chemical Society, of the Society of Chemical Industry, of the Institute of Chemistry, of the Society of Dyers and Colourists, of the Federal Council of Pure and Applied Chemistry, in fact of all relevant scientific societies, supported and greatly assisted by the advice and co-operation of the Royal Society. It would appear, therefore, that in the minds of those qualified to express an opinion, that it will redound to the national advantage in every way for the world to see what the British men of science have done and are doing to build up the

science of chemistry as it is known in the world to-day. That is the answer.

We may put it higher: The pure chemistry exhibit at Wembley will, without a doubt, for ever destroy the illusion, which had some justification in the past, that our university training and research in chemistry is below the highest standard of other countries.

This would not have been true in the same sense thirty years ago.

We have always had masters, giants of science. In a sense the exceptional man of genius and science belongs to the world. In the richness and the output of the many workers of talent, in the vigour of the teaching at the many universities, in the output of first-class work in every branch of chemical science, you find the true criterion of the national position in chemical science.

Thirty years ago we could not have shown this. The development of our chemical schools which we know to-day is comparatively new, and is as yet not appreciated by the general public. What is the importance of this?

It is of importance to the chemical industry for the world to know that behind it are great schools of chemistry, directed by great teachers of chemistry and inspired by great original workers in chemistry who can supply ideas and well-trained students to fertilise the chemical factories—otherwise arid wastes of pipes and tubs and vats and buildings.

It is also of importance to our university laboratories that their work and influence should be more widely known to the public who support them.

However, perhaps it has not occurred to everybody what an enormous advantage it is to the public to see with its own eyes and to be able to comprehend by the most charmingly delightful examples, things which were a few years ago entirely matters of metaphysical speculation. To quicken the imagination of our people, to give them some idea of the enormous interest—of which they are for the most part entirely unaware—of the simple things which surround their daily life, is one consequence of the result of this exhibit.

Nothing could be of greater importance than to give the general public, through the eye and in an interesting, fascinating way, greater appreciation of the value of chemical science in the affairs of life, and of the steps that precede great industrial or medicinal discoveries.



since he was able to isolate tri- and penta-acetyl, benzoyl, and other derivatives.

Investigations are in progress with the object of ascertaining whether this is the case with the other members of the series, and whether it is supported by all the experimental facts.

In the present communication, the simple formula,  $\alpha\text{-C}_3\text{H}_7\cdot\text{SnO}\cdot\text{OH}$ , has been adhered to, since it is possible to account for all the practical data presented in the experimental part.

When destructively distilled, the acid gave propyl alcohol, water, propylene and propane. The residue chiefly was stannous oxide, but stannic oxide was also present.

The decomposition may thus follow the three courses expressed by the equations:—  
 $\text{C}_3\text{H}_7\cdot\text{SnO}\cdot\text{OH} = \text{C}_3\text{H}_7\cdot\text{OH} + \text{SnO}$   
 $\text{C}_3\text{H}_7\cdot\text{SnO}\cdot\text{OH} = \text{C}_3\text{H}_6 + \text{SnO} + \text{H}_2\text{O}$   
 $\text{C}_3\text{H}_7\cdot\text{SnO}\cdot\text{OH} = \text{C}_3\text{H}_8 + \text{SnO}_2$

#### EXPERIMENTAL.

##### Preparation of $\alpha$ -Propyl-stannonic Acid.—

Sixteen grams of propyl bromide (or in some experiments 22 gr. of the iodide) were added to a solution of potassium hydrogen stannite, obtained by treating 20 gr. of stannous chloride mixed with 60 cc. of water, with enough of a cold 10 per cent. solution of potassium hydroxide (about 240 cc.) to dissolve completely the precipitate of stannous hydroxide first formed.

Alcohol (about 200 cc.) was added to make the mixture homogeneous. It was shaken at intervals during fourteen days.

The solution was then made almost neutral with dilute hydrochloric acid solution which was slowly added with stirring. The gelatinous precipitate was filtered off, washed with warm water until free from alkali, drained and dried.

When dry it was easily ground to a white amorphous powder.

On analysis—

0.8448 gr. gave 0.6480 gr.  $\text{SnO}_2$ ;  
 Sn = 60.5 per cent.

0.7008 gr. gave 0.2902 gr.  $\text{H}_2\text{O}$ , and 0.4647 gr.  $\text{CO}_2$ ;  
 H = 4.6 and C = 18.1 per cent.

$\text{C}_3\text{H}_7\cdot\text{SnO}\cdot\text{OH}$  requires Sn = 60, H = 4.1, and C = 18.5 per cent.

Propyl stannonic acid did not melt on heating, but decomposed in air at temperatures considerably above  $300^\circ$ , leaving a white residue of stannic oxide.

When destructively distilled out of contact with air, it gave a little propyl alcohol (oxidised by chromic acid to propionaldehyde), some water (which coloured anhy-

drous copper sulphate blue), a quantity of an unsaturated hydrocarbon (presumably propylene), and a small volume of a saturated hydrocarbon (propane). Much of the dark residue was soluble in a hot dilute solution of hydrochloric acid, yielding a solution of stannous chloride. The white insoluble residue was reduced to tin by heating in a stream of hydrogen, and was thus stannic oxide.

##### Properties of $\alpha$ -Propyl-Stannonic Acid.—

Propyl-stannonic acid was not soluble in water or any common organic solvent, except glacial acetic and other acids. It exhibited amphoteric properties, being soluble in both strong acids and strong solutions of the caustic alkalis.

*Potassium Propyl-Stannonate*,  $\text{C}_3\text{H}_7\cdot\text{SnO}\cdot\text{OK}$ .—The potassium salt of  $\alpha$ -propyl-stannonic acid was obtained by dissolving as much of the acid as possible in a warm 15 per cent. solution of potassium hydroxide. When cold, the supernatant liquid was placed in a vacuum desiccator over both concentrated sulphuric acid and sticks of potassium hydroxide.

After some days crystals of the potassium salt separated. These were washed several times with warm alcohol, to remove adhering potash, and dried.

On analysis—

0.4555 gr. gave 0.2920 gr.  $\text{SnO}_2$ ;  
 Sn = 50.5 per cent.

0.4555 gr. gave 0.1839 gr.  $\text{K}_2\text{SO}_4$ ;  
 K = 18.2 per cent.

$\text{C}_3\text{H}_7\cdot\text{SnO}\cdot\text{OK}$  requires Sn = 51.0 and K = 16.7 per cent.

Potassium propyl-stannonate was very hygroscopic, and was obtained free from excess of alkali only with difficulty. It was soluble in water, but the solution readily hydrolysed, being alkaline to indicators and giving a flocculent deposit.

The sodium salt was similarly obtained, and exhibited the same general properties as the potassium compound.

With solutions of calcium and barium chlorides, solutions of the alkali salts gave precipitates of the basic propyl-stannonates of these metals.

*Dipropyl tin oxide*,  $(\text{C}_3\text{H}_7)_2\text{SnO}$ .—Dipropyl tin oxide was obtained as a white precipitate by heating propyl-stannonic acid with excess of a ten per cent. solution of

potassium (or sodium) hydroxide, under a reflux condenser for several hours. The precipitate was filtered off, washed till free from alkali, drained, and dried.

On analysis—

0.2695 gr. gave 0.1837 gr.  $\text{SnO}_2$ ;

$\text{Sn} = 53.4$  per cent.

$(\text{C}_3\text{H}_7)_2\text{SnO}$  requires  $\text{Sn} = 53.8$  per cent.

The oxide did not melt on heating, but decomposed at high temperatures, leaving a residue of stannic oxide.

It did not dissolve in water, alkalis or organic solvents. Hot concentrated solutions of hydrochloric and hydrobromic acids dissolved it, forming the corresponding chloride and bromide.

*Propyl tin trichloride*,  $\text{C}_3\text{H}_7\text{SnCl}_3$ .—This compound was obtained by boiling propylstannonic acid under a reflux condenser with a benzene solution of hydrochloric acid gas.

When the resulting solution was evaporated in vacuo, colourless deliquescent prismatic crystals remained.

On analysis—

0.5050 gr. gave 0.2880 gr.  $\text{SnO}_2$ ;

$\text{Sn} = 44.93$  per cent.

0.5050 gr. gave 0.8224 gr.  $\text{AgCl}$ ;

$\text{Cl} = 40.3$  per cent.

$\text{C}_3\text{H}_7 \cdot \text{SnCl}_3$  requires  $\text{Sn} = 44.3$  and  $\text{Cl} = 39.5$  per cent.

The crystals of propyl tin trichloride were very soluble in water and most organic solvents. The aqueous solutions hydrolysed, especially on warming.

*Propyl tin tribromide*,  $\text{C}_3\text{H}_7 \text{SnBr}_3$ .—Propyl tin tribromide was obtained by dissolving the stannonic acid in concentrated hydrobromic acid. The substance possessed a darker colour than the trichloride, which it resembled in being deliquescent.

#### THE BRITISH CAST IRON RESEARCH ASSOCIATION.

The various researches detailed in previous announcements are progressing, reports upon same will be given in Bulletin No. 4, which is now being prepared.

*Semi-Steel*.—During the recent visit of Dr. Moldenke, of America, to this country, he expressed some very interesting remarks as to the manufacture and nomenclature of semi-steel. There is no doubt that a better name should be found for it, and there is equally no doubt that better methods of manufacture will have to be

adopted if its production and use are to progress. The Association has carried out numerous investigations for its members, and has collected a large amount of data upon the methods adopted by various makers. Although the Association are not yet in a position to state that definite conclusions have been arrived at, they can offer considered advice to its members upon the best melting practice to adopt. This has been done in many cases with the result that mixture and melting processes have been improved. When the Association has completed its investigation there is no doubt that it will be able to make such a report to its members as will enable them to produce a material that will be of widespread use.

*Supplying Pig Iron on Analysis*.—A circular giving recommendations for supplying pig iron on analysis has been circulated to the Blast Furnace Owners in this country by Dr. R. Moldenke and Mr. W. Wood, on behalf of the American Society for Testing Materials. The recommendations will be carefully considered by this Association in due course.

#### PROBLEMS SENT IN BY MEMBERS.

Several problems have been sent in during the past month for assistance by the Association, including the following:—Defective gas engine cylinder casting; mixture for cast iron permanent mould; nature of cast iron scrap for Cupola mixture; quality of ganister; corrosion of cast iron propellers.

#### GENERAL NOTES.

##### SAFEGUARDING OF INDUSTRIES ACT.

##### PART I.—ARBITRATIONS UNDER SECTION 1.

The Board of Trade has received formal notices of complaint under Sub-section (5) of Section 1, that

Rongalite,  
Sodium Formaldehyde Sulphoxylate,  
and

Zinc Formaldehyde Sulphoxylate  
have been improperly included in the lists of articles chargeable with duty under Part I. of the Act.

These complaints will be submitted in due course to the Referee appointed by the Lord Chancellor for the purposes of the Sub-section, and any person interested should communicate immediately with the Assistant Secretary, Board of Trade (Industries and Manufactures Department), Great George Street, London, S.W.1.

## DYESTUFFS (IMPORT REGULATION) ACT.

### APPLICATIONS FOR LICENCES IN OCTOBER.

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during October has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee.

The total number of applications received during the month was 520, of which 428 were from merchants or importers. To these should be added the 40 cases outstanding on October 1, making a total for the month of 560. These were dealt with as follows:—

Granted—423 (of which 381 were dealt with within 7 days of receipt).

Referred to British makers of similar products—75 (of which 63 were dealt with within 7 days of receipt).

Referred to Reparation supplies available—53 (all dealt with within 2 days of receipt).

Cancelled—1.

Outstanding on October 31, 1923—8.

Of the total of 560 applications received, 498, or 89 per cent., were dealt with within 7 days of receipt.

## CANADA'S NON-FERROUS METALS.

Canada exported during the twelve months ended September 30 last iron and products thereof valued at \$63,406,239, compared with the previous year's total of \$35,647,293. The total value of non-ferrous metals exported was \$57,169,208, as against \$32,831,376 for the preceding twelve months, and shipments of these included:

	Quantity.	Value.
	cwts.	\$
Aluminium, bars and blocks .....	167,439	3,059,445
Copper ore .....	351,128	3,469,307
Copper blister .....	431,719	6,042,835
Gold ore, dust, &c. ....	—	10,443,618
Lead .....	—	3,236,634
Nickel .....	561,508	10,080,020
	ozs.	
Silver ore and bullion .....	19,007,224	12,422,865
Zinc .....	—	2,556,332

### Non-Metallic Minerals.

Exports from Canada of non-metallic minerals during the twelve months ended September 30, 1923, amounted in value to

\$29,728,160, as against \$22,618,582, the total for the previous twelve months. They included:—

	Quantity.	Value.
	tons.	\$
Asbestos .....	203,762	8,339,485
Coal .....	1,807,973	11,510,343

## PROCEEDINGS AND NOTICES OF SOCIETIES.

### THE ROYAL SOCIETY.

THURSDAY, NOVEMBER 8.

Papers read:—

A. S. PARKES: *Studies on the Sex-ratio and related Phenomena—Fetal Retrogression in Mice.* Communicated by Dr. F. H. A. Marshall, F.R.S.

R. A. FISHER: *The Influence of Rainfall on the Yield of Wheat.* Communicated by Sir John Russell, F.R.S.

The Rothamsted data for rainfall and wheat yields extend to 1854; these data have been utilised to calculate the average effect on the yield of rain at different periods of the harvest year, for plots under 13 different manurial treatments. The method is an extension of the method of partial correlation, applicable when the number of independent variates is very large and can be arranged in a continuous series. This has involved the analysis of the distribution of rainfall in each of the years; a significant and progressive change has been in progress in the distribution of rain. The elimination of such slow changes and others which appear in the yields has been effected by the method of polynomial fitting; this method is shown to minimise the errors involved in such alternative processes as the use of Variate Differences.

The several plots show marked differences in their response to rain, showing that it is not impossible for the farmer to adapt his manurial treatment to a wet or dry season. A large part of the differences may be ascribed to the effects of loss of soil nitrates by percolation; other effects not susceptible to this explanation, and not hitherto anticipated, include the losses on the highly nitrogenous plots due to late summer rain. The residual value of artificial nitrogenous manures appears from

these results to be considerably greater than has been thought.

Paper read in title only:—

D. THURSBY-PELHAM: *The Placentation of Hydrax Capensis*. Communicated by Prof. J. S. Gardiner, F.R.S.

THURSDAY, NOVEMBER 15.

Papers read:—

SIR WILLIAM BRAGG, F.R.S., and PROF. G. T. MORGAN, F.R.S.: *Crystal Structure and Chemical Constitution of Basic Beryllium Acetate and Propionate*.

G. I. TAYLOR, F.R.S.: *Experiments on the Motion of Solid Bodies in Rotating Fluids*.

L. C. JACKSON: *Investigations on Paramagnetism at Low Temperatures*. Communicated by Prof. H. Kamerlingh Onnes, For. Mem. R.S.

L. C. JACKSON and PROF. H. KAMERLINGH ONNES, FOR. MEM. R.S.: *The Magnetic Properties of some Paramagnetic Double Sulphates at Low Temperatures*.

H. H. POTTER: *Some Experiments on the Proportionality of Mass and Weight*. Communicated by Prof. O. W. Richardson, F.R.S.

Papers read in title only:—

LORD RAYLEIGH, F.R.S.: *Further Studies on the Glow of Phosphorus and its Extinction by Moist Oxygen*.

PROF. H. A. WILSON, F.R.S.: *An Experiment on the Origin of the Earth's Magnetic Field*.

H. ROBINSON, D.Sc.: *The Secondary Corpuscular Rays produced by Homogeneous X-Rays*. Communicated by Sir Ernest Rutherford, F.R.S.

LT.-COL. J. W. GIFFORD (with an Introduction by PROF. T. M. LOWRY, F.R.S.): *Some Reractive Indices of Benzene and Cyclohexane*. Communicated by Prof. T. M. Lowry, F.R.S.

J. A. V. BUTLER: *A Note on "The Significance of the Electrode Potential"*. Communicated by Prof. J. W. McBain, F.R.S.

## ROYAL INSTITUTION.

A General Meeting of the members of the Royal Institution was held on November 5, Sir James Crichton-Browne, Treasurer and Vice-President, in the chair. The thanks of the members were returned to Mr. F. Coston Taylor, for his donation of one hundred guineas to the Research Fund, and to Mr. Robert Mond, for his gift of busts and medallions of Dr. Ludwig Mond, Cannizzaro, Liebig, Berzelius, and others; statuette of Sir James Dewar, and many portraits and photographs. The death of Professor Jules Violle, an honorary member of the Institution, was announced, and a resolution of condolence with the family was passed.

Mr. H. A. Gwynne, Professor J. C. McLennan, and Colonel H. G. Wait were elected members.

## THE PHYSICAL SOCIETY OF LONDON.

A meeting of the Society was held on Friday, November 9, at the Imperial College of Science, South Kensington.

A Demonstration of "Experiments on the Reproduction of Vowel Sounds" was given by Sir Richard Paget.

The following papers were read:—

*The Scattering of Light by Carbon Dioxide and Some Organic Vapours*, by PROF. A. L. NARAYAN, M.A. (presented by Lord Rayleigh).

*Measurement of the Surface Tension of a Small Quantity of Liquid*, by DR. ALLAN FERGUSON.

Proceedings of the meeting held on Oct. 26, Alexander Russell, M.A., D.Sc., in the chair:—

The President announced that Mr. F. E. Smith had been forced, owing to pressure of work, to resign his position as Honorary Secretary of the Society, and expressed the Society's warm appreciation of the value of the services he had rendered in that office.

The President further announced that Prof. A. O. Rankine had been elected by the Council to succeed Mr. Smith as Secretary.

Papers read:—

*The Fine Structure of Some Sodium Salts of the Fatty Acids in Soap Curds*, by S. H. PIPER, D.S.O., B.Sc., and E. N. GRINDLEY, B.Sc.

X-ray photographs of certain sodium salts of the fatty acids (soap curds) show lines due to reflections from planes with very wide spacings of the order 40 A.U. These planar spacings increase uniformly with the number of  $\text{CH}_2$  groups in the molecule, indicating an effective length of 1.25 A.U. for the  $\text{CH}_2$  group. These and other lines can be accounted for by assuming that the curds are in the smectic state described by Friedel.

#### Discussion.

Mr. G. Shearer said that in conjunction with Dr. Miller he had recently been examining compounds somewhat similar to those referred to in the paper, with similar results. The compounds he had dealt with were, however, solids, namely the heavier fatty acids and their esters. He also had found a regular increment in the spacing for each  $\text{CH}_2$  radicle added, and his observations confirmed the supposition that the axes of the molecules are perpendicular to the strata in which they lie. The experiments are of special interest in that they measure the actual length of one or of two molecules. He congratulated the authors on the excellence of their photographs for a semi-liquid substance, which were exhibited at the meeting.

*X-Ray Analysis of Solid Solutions*, by E. A. OWEN, M.A., D.Sc., and G. D. PRESTON, B.A.

The atomic structure of solid solutions of copper-aluminium, aluminium-magnesium, and copper-nickel has been examined by the X-ray spectrometer. In each case it was found that the solute atom replaces an atom in the lattice of the solvent, the substitution being accompanied by a distortion of the lattice.

A saturated solution of aluminium in copper shows that the aluminium expands the copper lattice from 3.60 A to 3.65 A. The effect of adding nickel to copper was to produce a contraction of the lattice, the contraction being approximately a linear function of the atomic percentage of either constituent. The addition of 8 per cent. magnesium by weight to aluminium causes the average parameter of the aluminium lattice to increase from 4.05 A to 4.10 A. The addition of 8 per cent. aluminium by weight to magnesium decreases the average parameter of the hexagonal lattice of mag-

nesium from 3.17 A to 3.15 A, and increases its axial ratio from 1.63 to 1.66.

An examination of the eutectic alloy of aluminium and copper showed that this alloy consists of a mixture of two distinct substances with different space lattices. The one substance being  $\text{Cu Al}_2$  and the other a substance the space lattice of which could not be distinguished from that of pure aluminium.

The intermetallic compound  $\text{Cu Al}_2$  was found to possess a simple tetragonal lattice of side 4.28 A and axial ratio 0.562, the copper atoms being at the corners and the aluminium atoms at the centres of the four small faces.

The atomic structure of the compound  $\text{Cu Al}$  resembles that of a solid solution of aluminium in copper, but the distortion is considerably greater. The material was found to have a face centred trigonal lattice of side 3.89 A and an angle between the axes of  $94.6^\circ$ , the 111 planes being composed alternately of aluminium and copper atoms.

#### Discussion.

Mr. F. Twyman commented on the fineness of the definition in X-ray photographs, remarking that it might have been expected that owing to penetration of the rays into the material and from other causes, considerable blurring would occur, yet the lines shown are not more than a hundredth of an inch wide.

Dr. E. A. Owen, in reply, said that the good definition might be ascribed (1) to the fact that the rays do not penetrate to any great depth in the reflecting material, owing to their being almost completely reflected by the outer layers of atoms; and (2) to the well-known focussing effect obtained when the photographic plate and the source of radiation are equidistant from the reflecting surface.

*Cohesion*, by HERBERT CHATLEY, D.Sc., A.INST.P.

The paper traced the consequences of assuming that the alternately positive and negative atoms in a crystal may be treated as doublets attracting according to an inverse fourth-power law, while the electron fields surrounding the atomic nuclei repel according to an inverse tenth-power law. It is shown that the numerical results agree fairly well with the facts as regards the strain which produces rupture in solids, and

as regards the rate of change of compressibility with compression in liquids.

#### Discussion.

Prof. A. O. Rankine said that while he recognised that the numerical results of the theory were fairly consistent with experimental values, he could not help suspecting that this was a coincidence. What little is known of the nature of cohesion seems to indicate that the laws concerned must be far more complicated than a simple inverse power law. The doublets would only attract according to an inverse fourth-power law at a distance great compared with the distance apart of their components, not at the distances which actually obtain in a crystal; and, again, in a crystal the electron swarms of neighbouring atoms must be very close to one another in certain regions, and it is difficult to see why the particular law adopted in the paper should hold. Further, the field of force round an atom must be regarded as having an axis, not as being spherically uniform and independent of direction. It seems unsatisfactory also to test a theory based on the structure of a solid crystal by measurements made on water in the liquid state.

Dr. D. Owen said that, while agreeing with the previous speaker that the formulæ proposed in the paper were open to objection, any hypothesis seemed better than none. Calculations such as the author had made might be of value in suggesting limiting values of elasticity and density under great stresses; they permitted, for example, of interesting speculations as to the conditions of matter deep in the earth's interior.

#### THE FARADAY SOCIETY.

Papers read at the meeting on November 12:—

Part I.—*The Electrodeposition of Manganese*, by A. J. ALLMAND and A. N. CAMPBELL.

The problem of the cathodic deposition of manganese from aqueous solution has received little attention in the past. Bunsen states that he obtained the metal by electrolysis of aqueous manganous chloride solutions, using the apparatus employed in the deposition of chromium. The metal was deposited as sheets 1 sq. cm. in area; it was metallic looking, and oxidised almost as

rapidly as potassium. If the current density were reduced, manganomanganic oxide came down. Moore states that metallic manganese may be deposited as such from a neutral solution containing a large excess of ammonium sulphocyanide; a powerful current is necessary. Smith and Frankel find that, if an excess of potassium sulphocyanide be present, the metal comes down in greyish-white compact form. Under the conditions specified, the current must be low. The metallic deposit is inclined to oxidise rapidly. Van Arsdale and Meier give results of some experiments conducted on the electrolysis of manganese sulphate solutions. These will be referred to in more detail below, as they were to a large extent repeated by the present authors, to whom the paper was unknown when the work was started. Finally, Forster quotes some results obtained by Grube, who states that very pure manganese can be obtained by electrolysis of a 6-7 N.  $MnCl_2$  solution, separated by a diaphragm from the anode. The electrolyte is also 1.5 N. with respect to  $NH_4Cl$  and 0.1 N. with respect to  $HCl$ . The current density is 20 amps./d.m.<sup>2</sup> The electrolyte is strongly stirred, and its temperature 30°. The current efficiency is said to be between 50 and 60 per cent., and the purity of the deposit 99.9 to 100 per cent. "There is a marked tendency for the deposit to sprout at the edges of the cathode, as a result of the high current densities used. This can, however, be overcome by arranging that the cathode fills the whole cross-section of the cell, and manganese is then obtained as a smooth microcrystalline deposit, which can be removed from the copper cathode in the form of coherent sheet." In later papers Grube and Metzger refer to sheets of metal 1 mm. thick made by this method.

The problem then was the working out of the conditions for the successful electrodeposition of a highly electropositive metal from aqueous solution. We decided in the first instance to use as electrolytes simple manganese salts. It could be predicted in advance that the electrolysis would be favoured by a high metallic salt concentration and by a low hydrogen ion concentration. A high current density was also likely to be advantageous. With regard to temperature, the matter was more complex. To take extreme cases, if manganese were a metal like zinc, with high hydrogen overvoltage and small irreversible resistance to cathodic deposition, a low temperature



would be better; if like iron, with small hydrogen over-voltage and large irreversible cathodic effects, then high temperatures would be better. We commenced on the supposition that it would behave more like iron than like zinc, a view which turned out to be only partly correct, as both high hydrogen over-voltage and high irreversible resistance to manganous ion discharge were found.

It was found that the effects of changes in composition of electrolyte, current density, temperature, and type of cell influenced the deposition.

Pure manganese in coherent form can be prepared in small quantity with a current efficiency of 40-50 per cent.

Attempts to prepare larger amounts in coherent form have so far been unsuccessful.

A large number of experiments were carried out with the object of improving the deposit in view, without any striking success.

A variety of addition agents were tried, using the standard manganese sulphate and ammonium sulphate electrolyte. None produced any marked improvement, and in several cases (*e.g.*, gum arabic, dextrine, gelatine) the deposit was made much less pure.

With the same electrolyte, an experiment was done, making use of a burnisher (an ebonite strip) pressed against the rotating cathode. The deposit obtained was smooth and dense, but the current efficiency was reduced to 8.6 per cent.

Other electrolytes were tried. The use of sulphocyanide gave a more coherent but less pure deposit. The use of a mixture of manganese and ammonium perchlorates also led to nothing, as the whole catholyte hydrolysed with great rapidity, becoming filled with manganous hydroxide.

Further experiments are being carried out.

*The Cathodic Behaviour of Alloys.*—Part I.: *Iron—Nickel Alloys*, by S. GLASSTONE, M.Sc., Ph.D., University College, Exeter.

Very little work has been done on the measurement of polarisation voltage at electrodes composed of metallic alloys, and therefore investigations were undertaken with the hope of throwing some light on the problem of over-voltage and allied phenomena. In working with alloys that are prepared from a fused mixture of the metals, the structure, and no doubt the properties

of the alloy as an electrode, will depend upon the method of cooling. Further, the surface skin will probably be different from the rest of the alloy. The object of this work was to investigate the cathodic behaviour of alloys, as well as the electrolytically deposited pure metals for comparison, along three lines: (1) to measure the cathodic potential during deposition from a solution of mixed salts, (2) to determine the potential required for hydrogen liberation in sulphuric acid and sodium hydroxide solutions, *i.e.*, "over-voltage," and (3) to investigate the action of depolarisers. Schlötter has shown that the reduction efficiency of any particular cathode in potassium chlorate solution is greatly influenced by depositing upon it traces of another metal in amounts insufficient to cover the surface of the cathode completely. Thus the system electrode metal—deposited metal—hydrogen might be more or less efficient for the purposes of reduction than the original electrode system before metal deposition. Since an alloy at which hydrogen is being evolved as a result of electrolysis, resembles to a very great extent the electrode system used by Schlötter, it appeared that a systematic investigation of the cathodic behaviour in the presence of depolarisers would be of considerable interest.

Examination of the cathodic behaviour of iron-nickel alloys, deposited from solutions of varying proportions of ferrous and nickel sulphates, from several standpoints has brought to light a number of new facts concerning their electrode deposition, over-voltage and action in the presence of depolarisers. Suggestions have been offered to account for some of the observed facts, but a fuller discussion of their significance in connection with the theories of over-voltage, delayed cathodic deposition and of cathodic reduction, must be left until further information is available.

*The Volumes Occupied by the Solute Atoms in certain Metallic Solid Solutions and their Consequent Hardening Effects*, by A. L. NORBURY, M.Sc., University College, Swansea.

The object of this research was to determine the densities of certain copper  $\alpha$ -solid solution alloys, to calculate the volumes that the solute atoms were occupying in each case, the ultimate object being to compare the values so obtained with the hardness values of the same alloys.

In order to obtain accurate values, the

effects of annealing temperature and cold-work on the density of copper were first studied. The densities of the copper  $\alpha$ -solid solutions were then determined, and the results calculated in a certain manner in order to estimate the "atomic volumes" occupied by the solute atoms in each case.

The results obtained were then compared with the hardness values, and a certain relationship was brought out. It was also found that the solute atoms were not occupying their normal atomic volumes, but that in each case a contraction or expansion had taken place—the amount of contraction or expansion apparently increasing as the "chemical affinity" of the solute for the solvent increased.

The paper dealt with the method of determining densities; the effect of annealing temperature and cold-work on the density of cathode copper; the density of commercial copper, and of certain copper  $\alpha$ -solid solutions. It also included the calculation of "mean atomic volumes" and comparison of the latter with hardness data, and suggested an explanation of hardening effects of elements in solid solution.

In density determinations errors due to surface-tension effects between the surface water and the suspending wire were eliminated by the use of a compensating platinum wire.

Cold-hammering had the effect of closing up minute blow-holes in copper. Very severe cold-hammering set up stresses and strains in the metal which probably caused local increases and decreases in density. Otherwise cold-hammering did not affect the density.

Commercial copper has a distinctly lower density than cathode copper.

For theoretical purposes there are certain advantages in calculating density results as "mean atomic volumes."

When an element is distributed in solid solution as single atoms replacing single atoms of the solvent in the space-lattice of the latter, the hardening effect is, in general, proportional to the difference in size of the solute and solvent atoms. The above relationship does not, however, hold in certain exceptional cases (*viz.*, Si in Cu and Na in Pb), which appear to arise when the solute has an exceptionally strong "chemical affinity" for the solvent. In such cases it is suggested that the solute exists in solid solution in the form of molecules of an inter-metallic compound having a different space-lattice from that of the solvent. The

interference with slip and consequent hardening being relatively much greater in this type of solid solution.

When an element forms a solid solution with another element, there is a certain contraction or expansion which seems to be large or small according to whether the "chemical affinity" between the elements is large or small.

From the theoretical point of view it was thought interesting to ascertain whether cold-hammering increased the hardness of each of the solid solutions to the same extent.

The solid solutions were therefore reduced first 60 per cent. in thickness and later 90 per cent. in thickness and their hardnesses measured after each reduction.

It was difficult to hammer all specimens to exactly the same amount, and this factor makes the results somewhat erratic; they seem, however, to be sufficiently accurate to show that the nickel-copper solid solutions have hardened relatively less than any of the other solid solutions, which appear to have hardened to equal extents.

*The Catalytic Decomposition of Hydrogen Peroxide Solution by Blood Charcoal*, by J. B. FIRTH, D.Sc., and F. S. WATSON, M.Sc.

Hydrogen peroxide has been shown to be decomposed by a great variety of substances. Fillipi showed that all powders decompose hydrogen peroxide, the velocity of decomposition being proportional to the exposed surface of the added powder and independent of the concentration of the hydrogen peroxide. Lemoine found that charcoals obtained in the decomposition of wood, coconut and sugar are efficient catalysts of hydrogen peroxide; the catalytic effect being apparently correlative with their sorptive power for gases. Clayton showed that hydrogen peroxide does not volatilise appreciably from its aqueous solutions at 50° to 60° C., and the rate of decomposition is not affected by stirring. Rideal and Thomas show that hydrogen peroxide is decomposed by Fuller's earth. The catalytic activity in the decomposition of the hydrogen peroxide is not dependent on the adsorptive power; it would appear that the iron content of the Fuller's earth may be the governing factor. On applying the equation for a unimolecular surface reaction the velocity coefficient is constant for a given sample of Fuller's earth. The authors have shown that ordinary pure sugar carbon gives rise to only

very slight decomposition of hydrogen peroxide in aqueous solution, but the rate and extent of the decomposition increases considerably as the activity of the carbon is increased, and also with rise of temperature. The activity of the carbon gradually decays during the reaction. In a further paper the authors described experiments with specimens of carbon from other carbohydrates in which it was shown that the rate of decomposition varied considerably with the different carbons, but the fundamental difference is in the initial activity. The activity falls rapidly after the first few minutes, becoming ultimately very slight, even though the solution contains a fair proportion of undecomposed hydrogen peroxide. The object of the present investigation was to study the decomposition of hydrogen peroxide solution by blood charcoal, before and after activation treatment. Whereas in previous experiments relatively pure carbons were used; in the present case the charcoal contains appreciable quantities of impurity, mainly iron. Experiments were therefore carried out in order to determine as far as possible the influence of this impurity on the rate of decomposition of the hydrogen peroxide.

The blood charcoal used gave 8.82 per cent. of ash which consisted almost entirely of iron oxide. After treatment with hot aqua regia, the ash content was 7.30 per cent. It was then subjected to treatment with aqua regia for a month, the ash content becoming 6.32 per cent. Some of this charcoal was further treated with bromine for several days, after which the ash content was 5.79 per cent. In each case all soluble material was extracted by washing with boiling distilled water until the filtrate showed no indication of iron or halogen.

A sample of the charcoal was taken after each purification process. It was dried at 120° C. in an air oven, and the catalytic activity determined in each case. The hydrogen peroxide solution used contained 240.5 cc. of available oxygen per 25 cc. of solution. 0.25 grams of the charcoal and 25 cc. of the hydrogen peroxide solution were used in each experiment, and the temperature of experiment 18° C. The reaction velocity coefficients were calculated from the equation for a unimolecular surface reaction  $dx/dt = K(a - x)$  to the Napierian base and the minute as unit of time.

The charcoal showed moderate catalytic activity in the decomposition of hydrogen peroxide solution.

This was considerably increased by previous heating in a vacuum at 600° C. and 900° C., and was still further increased by previous sorption of iodine from solution and from which the iodine had been subsequently completely removed.

The activity of an activated charcoal consists of two types, one which is termed  $\alpha$  activity which is very rapid, but ceases after a few minutes, and a second termed  $\beta$  activity, which may persist for several hours. Both types may be increased by activation methods. In ordinary blood charcoal  $\alpha$  activity is absent.

The introduction of iron into sugar solution prior to carbonisation considerably increased the activity of the charcoal, by an amount, greater than can be accounted for, by the iron alone, and it is suggested that the iron acts as a spacing agent thereby increasing the activity of the carbon itself.

The velocity of decomposition was shown to vary with the concentration of the hydrogen peroxide solution.

The proportion of hydrogen peroxide decomposed was determined by both the activity of the charcoal and the concentration of the hydrogen peroxide solution.

In the case of the highly active carbons, the heat generated by the rapid decomposition of the hydrogen peroxide raised the temperature of the reaction, temporarily, by several degrees, which further facilitated the decomposition of the hydrogen peroxide and thereby maintained the velocity of reaction at a higher level, until this heat had been dissipated.

*The Properties of Powders.—Part VIII. : The Influence of the Velocity of Compression on the Apparent Compressibility of Powders, by E. E. WALKER.*

When a powder is compressed in a cylinder by a constant load, the velocity of compression is very high to begin with and then rapidly falls off, but no case has been observed so far where it falls off to zero before the powder is completely compressed.

This has now been investigated. Observations were made on the height of the plunger after various intervals of time, the load being kept constant. As a rule the load was applied by means of a small Tange press, and kept constant by manipulation of the hand-operated oil pump—but in certain cases where it was necessary to keep the load constant for several hours a dead load was employed. The load was applied as rapidly and gently as possible, and zero

time taken from the moment at which the full load was applied. On account of errors arising from the estimation of zero time, observations made in less than 20 seconds were liable to considerable error.

The isobaric curve has been correlated with the value of the ratio:—

resistance to impact

resistance to static load

and further evidence for the validity of the classification of powders suggested in Part VI. of these studies has been obtained.

The exceptional readiness with which powdered ammonium nitrate shrinks has been shown to be dependent chiefly on the high value of its velocity coefficient.

The powders examined were shown to fall into three classes.

Substances in Class I. are regarded as normal substances, which are compressed by deformation of the particles both when static loads are employed and when compression is brought about by the impact of falling weights.

Substances in Class II. are regarded as behaving normally when they are compressed slowly by static loads, but when the compression is brought about suddenly by blows the particles are broken down into fragments which fall together into closer order, so that the resistance to compression is much less than the calculated value to begin with. As compression proceeds further disintegration takes place, causing an increase of resistance analogous to the hardening of metals by cold working.

In Class III. conditions are exceedingly complex since disintegration is caused both by slow and by rapid compression (impact), and accordingly there is no connection between calculated and observed values. Calcium carbonate is an example of this total lack of agreement.

*An Investigation of Smoluchowski's Equation as Applied to the Coagulation of Gold Hydrosol*, by LEONARD ANDERSON, B.Sc., Ph.D.

As regards the kinetics of coagulation of colloidal solutions the Smoluchowski equation is the only one which has a theoretical basis. Freundlich deduced an equation, based on measurements of the variation of the viscosity of a sol during coagulation, giving the relationship between time and the amount of precipitated colloid. However, no definite relationship is known to

exist between the size of particles and viscosity.

According to Smoluchowski's theory, each particle in a homogenous sol possesses a sphere of attraction  $R$ , within which the attraction is so strong that any other particle, whose centre enters this sphere, is firmly held.

In an originally uniform sol, whose particles have been completely discharged, the initial number of particles whose centres are less than  $R$  apart is vanishingly small.

In course of time, Brownian movement brings the particles into all possible configurations. In consequence of Brownian movement and of the existence of "spheres of attraction" an irreversible state of coagulation is finally set up.

Smoluchowski, combining probability considerations and the laws of diffusion, derives a series of equations which give the rate of disappearance of the particles in a colloid solution during "rapid" coagulation. The following equation gives the rate of disappearance of primary particles:

$$v_1 = \frac{v_0}{(1 + \beta t)^2}$$

where  $v_0$  is the number of primaries at zero time,  $v_1$  is the number of primaries at a time " $t$ ," and  $\beta$  is a constant equivalent to  $4\pi DRv_0$ , where  $D$  is the diffusion coefficient and  $R$  is the radius of the sphere of attraction.

Smoluchowski also attempted to extend his theory to slow coagulation. Colorimetric determinations of the rate of coagulation of gold sols by HCl, KCl, BaCl<sub>2</sub>, and AlCl<sub>3</sub> were carried out using Hatschek's method.

These experiments now brought forward indicate that in the coagulation of gold sols, by means of the electrolytes chosen, there is a "rapid" region in which Smoluchowski's equation holds. The constancy of  $\beta$  is quite good, especially in the case of barium chloride as electrolyte. In a region of smaller electrolyte concentration, an excessive slowing down in the speed of coagulation with time is observed. This is in agreement with the data of Kruyt and Arkel and also with the one case of Mukherjee and Papaconstantinou in which the value of  $\beta$  falls.

The general conclusion arrived at is that the Smoluchowski equation is strictly limited in its application.

Smoluchowski asserts that the curves depicting slow and rapid coagulation should

have a similar form, the only varying factor being the probability that an impact will give union.

The data obtained, however, show that coagulation proceeded even more slowly than would be expected on the basis of a bimolecular process. Furthermore, if primaries did disappear simply by union with each other, it would follow that once coagulation has commenced it should proceed until no more primaries are left. On this basis incomplete colour change from red to blue should not be possible, since any red colour remaining would indicate unchanged primaries (attributing the red colour to the latter). But incomplete colour change does occur and depends upon the concentration of the electrolyte present. This phenomenon admits of two explanations:

1.—It may be due to the possibility that the rate of disappearance of primaries is counterbalanced by an opposing effect, i.e., primaries are being reformed either by spontaneous disruption of complexes or by collision of complexes with each other. Such reversibility, however, would seem to entail a behaviour, on dialysis, of incompletely coagulated sol which has not yet been observed.

2.—A more probable explanation would seem to be that the initial primary particles (giving the red colour) are *unequally* charged. In the case of slow and eventually incomplete coagulation very small amounts of electrolyte are used, and it is conceivable that the amount adsorbed is not sufficient to reduce the charge of some of the particles (which initially carry an excessive charge) below the critical limit which will permit coagulation to take place.

If this conception of unequal charge is correct, the Smoluchowski equation could not be expected to be applicable in general.

In reviewing the whole problem of coagulation, it would appear that the Smoluchowski equation in its present form is limited in its application. Before it can be applied to all types of coagulation it apparently requires modification to allow for the two factors:

(a) The decrease of the probability factor as coagulation proceeds.

(b) The existence of incomplete coagulation as a consequence of unequal, and in some cases therefore, of excessive initial electrical charge on the primary particles.

(To be continued next week.)

## THE CHEMICAL SOCIETY.

ORDINARY SCIENTIFIC MEETING,

THURSDAY, NOVEMBER 15.

The following papers were read:—

*Ring-chain Tautomerism. Dynamical Evidence relating to the Mutarotation of the Sugars*, by J. W. BAKER, C. K. INGOLD, and

J. F. THORPE.

*The additive Formation of Four Membered Rings. Part III.—A system of Nomenclature for Heterocyclic Four Membered Rings and the Formation and Properties of some Derivatives of  $\beta$ -methylenedimineoxide*, by C. K. INGOLD.

## THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The seventy-third general meeting was held at the house of the Royal Society of Arts, on Tuesday, November 13. The fol-

lowing paper was read:—

*Galician-Canadian Pole Tool Fishing Methods*, by ALBERT MILLAR, A.M.I.MECH.-E., M.INST.P.

## THE ROYAL SOCIETY OF ARTS.

On Monday, November 12, the Cantor Lecture (I.), entitled *The Cultivation of Cocoa in British Tropical Colonies*, was delivered by MR. SAMUEL HENRY DAVIES, M.Sc., F.I.C.

At the Ordinary Meeting, on Wednesday, November 14, a lecture entitled *Téléphotographie, Télautographie, Télévision (Avec Expériences et Projections)*, was delivered by MONSIEUR EDOUARD BELIN (in French). Mr. Alan A. Campbell Swinton, F.R.S., late Chairman of the Council, presided.

The Royal Society of Arts, which was founded in 1754 for the encouragement of arts, manufactures and commerce, held the opening meeting of the 170th session on Wednesday evening, November 7, when Lord Askwith, K.C.B., the Chairman of the Council and a Vice-President of the Society, delivered his address on *Exhibitions*.

For the subsequent meetings before Christmas the following arrangements have been made:—

November 21.—J. A. KNOWLES, *Forgeries of Ancient Stained Glass*. The Earl of Crawford and Balcarres, K.T., P.C., will preside.

November 27.—THE VISCOUNT BURNHAM, C.H., LL.D., D.LITT., M.A., *The West Indies*.

November 28.—SIR HENRY JOHN GAUVAIN, M.A., M.D., M.Ch., Medical Superintendent of the Lord Mayor Treloar Cripples' Hospital, *The Effect of Sun, Sea and Open-air in the Treatment of Disease*. The Rt. Hon. Arthur Neville Chamberlain, M.P., will preside.

December 5.—ARTHUR WILLIAM HILL, M.A., Sc.D., F.R.S., F.L.S., Director of the Royal Botanic Gardens, Kew, *The Work of the Royal Botanic Gardens, Kew*. Charles Albert Seward, M.A., F.R.S., F.G.S., F.L.S., Professor of Botany at the University of Cambridge, will preside.

December 7.—WILLIAM FOSTER, C.I.E., B.A., Registrar and Superintendent of Records, India Office, *The Archives of the Honourable East India Company*. (Sir George Birdwood Memorial Lecture.)

December 12.—SIR FRANK BAINES, C.B.E., M.V.O., Director of Works, H.M. Office of Works, *The Preservation of Historic Buildings and Ancient Monuments*. Sir Aston Webb, K.C.V.O., C.B., P.R.A., will preside.

December 17.—WILLIAM C. NOXON, Agent-General for Ontario, *Emigration within the Empire*.

### CORRESPONDENCE.

#### NATIONAL CERTIFICATES IN CHEMISTRY.

To the Editors of THE CHEMICAL NEWS.

SIRS,—About three years ago the Board of Education established with the Institute of Chemistry a joint committee for the purpose of granting, under conditions, National Certificates in Chemistry to students in technical schools and colleges. These certificates are Part-time Course Certificates, (1) Ordinary, (2) Higher, and Full-time Course Certificates in (a) Chemistry, (b) Applied Chemistry. An institution wishing

to prepare students for any of these certificates must submit schemes of its own, which its students must follow. This seems a clumsy feature of the arrangement. Every institution devises its own scheme or schemes, sets the examination papers at the end of the course, and marks the scripts by means of its own teachers, the joint committee, having previously approved of the local schemes, finally appearing as assessors, who supervise the questions set, revise the marking of the papers, satisfy themselves about the laboratory work done by the candidates, and finally issue certificates to those who are successful.

All this is in accordance with the apparent policy of the Board of Education to make technical schools quite local in their character, and to encourage them to cater specially for the technical needs of their locality. Hence, the idea of a separate scheme from each institution has been evolved.

This policy of localisation does not satisfy the best type of students in the technical schools, who are not able to express their wants. Localisation does not tend to promote good general education, nor does it give students a wide outlook.

The students in the technical schools are there voluntarily. For various reasons they are not able to pursue their education in the day-time. They get their education in their spare time, generally after a day's work, and large numbers attain responsible positions and become as efficient as those who have done full-time work.

Such earnest students develop a longing for some distinction, in the form of a degree or diploma, the value of which is well-known and recognised all over the country. From my personal acquaintance I know that many look with longing eyes at London University degrees, but they are met with the stumbling block that they did not matriculate at the outset. For those in chemical trades there is the Institute of Chemistry, whose Fellows and Associates have a recognised standing. Spend what time they may in a technical school, study what subjects they may, make themselves as efficient as they may, all their work does not lead in the direction of a recognised distinction. True it is that certain institutions provide training in the evening which is recognised by the Institute of Chemistry, but they are situated in only 13 large towns in England and Scotland (not in Wales). What are the prospects of students else-

where? They are in a local groove, with no chance of getting out. The National Certificates, after all, are only local certificates, blessed by the Joint Committee, with an implied intimation, not an open one, that the holders are in a class to themselves, in which they must remain, because there is no intimation anywhere that a certificate can be used by the holder towards gaining any further qualification.

An opportunity has been missed of furthering the cause of education by assisting those students who will work if properly directed and encouraged.

Something should be done. The Institute of Chemistry already recognises evening training in 19 institutions. Let the Institute say that, *providing a student has previously passed an approved preliminary examination*, the subsequent gaining of one or more national certificates shall be regarded as so much training towards the qualification for the associateship. What would be the effect upon students in technical schools? It would be an incentive to those who do not possess it, to work first of all for an approved preliminary certificate, which alone would do their general education some good. Technical school students often lack a good general education. They are so eager to get on to trade work that they neglect a continuation of school work. Having passed an approved preliminary examination which the Institute will accept, the student could work for such National Certificates as his particular technical school is approved for, fully knowing, and thereby encouraged, that any certificate gained will be a step towards a coveted qualification. If he finds that subsequently the varied chances of life bring him within reach of an institution on the Institute of Chemistry's recognised list, he could take advantage of it, knowing that his previous work will secure some remission from the four or five years' period now required.—Yours, &c.,

A.P.

November 5, 1923.

### THE PREPARATION AND PROPERTIES OF SILVER STIBIDE.

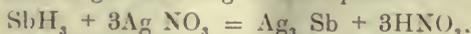
To the Editors of THE CHEMICAL NEWS.

SIRS,—Silver stibide has been known since the year 1896 by the existence of an angle on the cooling curve of silver antimony alloys (Henri Gautier, *Comptes Rendus*, 1896, CXXIII., 172-174). C. T. Hey-

cock and F. H. Neville (*Proc. Roy. Soc.*, 1896, X., 160-164) deduced evidence definitely giving it the formula  $\text{Ag}_3\text{Sb}$ .

In 1910 Th. Liebisch (*Sitzungsber. Akad. Wiss., Berlin*, 1910, 365-370) found that most specimens of silver stibide from Andreasberg corresponded to the formula  $\text{Ag}_3\text{Sb}$ . The mineral dyscrasite ( $\text{Ag}_2\text{Sb}$ ) crystallises in the rhombic system, and its colour is silver white. On exposure to air and light it acquires a dull grey or yellow colour.

In a previous paper by the author (*Chemical News*, 1923, CXXVI., 275) it was shown that stibine could be detected by passing it through some concentrated silver nitrate. If this is performed, using dilute silver nitrate in the cold, then the action is found to go according to the equation:—



The silver stibide formed was filtered off, washed and dried, when it was obtained in the form of silver white crystals, which crystallised in the rhombic form.

The properties of silver stibide are remarkable by the fact that it is totally insoluble in both hot and cold, concentrated and dilute, sulphuric and hydrochloric acids. It is, however, soluble in boiling dilute nitric acid, giving off nitrous fumes, but is insoluble in the cold dilute acid.—Yours, &c.,

EDWARD J. WEEKS, M.Sc., F.C.S.

East Dulwich, S.E.22.

### NOTICES OF BOOKS.

*Oil Facts and Figures*, October, 1923. Pp. 62. London: F. C. Mathieson & Sons, 16, Copthall Avenue, E.C.2. 1s. 6d.

This book contains a list of the producing oil companies, with the area and situation of the oil fields and the number of wells.

Besides the usual financial details, it gives the end of the financial year and the highest and lowest prices of shares for the years 1920 to (mid-October) 1923. The monthly output of a number of companies is contained in a separate table.

The large amount of information in a small volume makes it a valuable pocket reference book. Future editions might also indicate to which combine any particular company belongs. G.H.M.

### BOOKS RECEIVED.

*Practical Mathematical Analysis*, by H. VON SANDEN, with examples by the trans-

lator, H. LEVY, M.A., D.Sc., F.R.S.E. Pp. XI. + 195. 1923. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C. 10s. 6d. net.

*Die Atomic*, von JEAN PERRIN, mit autorisation des Verfassers deutsch herausgegeben von DR. A. LOTTERMOSER. Pp. XX. + 213. 1923. Verlag von Theodor Steinkopff, Residenzstrasse, 12b, Dresden, Blasewitz. 5s.



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*Latest Patent Applications.*

- 26736—Bhopal Produce Trust, Ltd.—Recovery of oxolates, etc. Oct. 25.  
 26572—British Cellulose & Chemical Manufacturing Co., Ltd.—Treatment of cellulose acetate, etc. Oct. 24.  
 26526—Henshaw, S.—Production of neutral sulphate of ammonia. Oct. 24.  
 26680—Leigh, R.—Hampers for acid carboys, etc. Oct. 25.

*Specifications Published this Week.*

- 205224—Houseman, C. R., and British Oxygen Co., Ltd.—Manufacture of sulphur dioxide and apparatus for use therein.

*Abstract Published this Week.*

- 203352—Titanium oxide and sulphate.—Weizmann, C., and Blumenfeld, J., of 16, Addison Crescent, London.

*Titanium sulphate and oxide; ferrous sulphate.*

—To obtain titanium compounds free from iron, an ore such as ilmenite is heated to 150-180° C. with sulphuric acid of 70-90 per cent. strength. The solid product is leached with a limited quantity of water in presence of a reducing agent, preferably spongy iron, most of the iron sulphate being left in the solid form. The water is added little by little at a temperature not above 50° C. The reduction is completed when a brown-violet coloration shows the presence of titanous salts. The solution is then treated to hydrolyze the titanium sulphate in any known way, and the first washings of the precipitated hydroxide are effected with water acidulated with sulphuric acid and containing a titanous salt so as to avoid any oxidation of ferrous salts which would injure the colour of the product. The precipitate is calcined under oxidizing conditions, for instance by blowing air through the container or through the material during calcination, or, according to the Provisional Specification, by calcining in the presence of sulphuric acid, the object being to prevent any reduction owing to organic matter that might be present. The ferrous sulphate left with the undissolved residue of the ore is recovered by solution and crystallization, and may be treated to recover the sulphuric acid. According to the Provisional Specification, the solution of titanium sulphate is protected from oxidation during hydrolysis by means of a film of oil, vaseline or the like.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

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# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3319.

## THE INTERMITTENT GLOW OF PHOSPHORUS.

By K. R. KRISHNA IYER.

The intermittent luminosity propagated in pulsatory fashion when the last traces of oxygen are being removed from air by means of phosphorus, or when air is allowed to leak slowly into an exhausted vessel containing phosphorus, was recently dealt with by the present Lord Rayleigh (*Proc. Roy. Soc.*, 1921 (A) XCIX., 372). He showed the importance of the presence of water vapour for the propagation of the luminous pulses, and also how the same phenomenon occurred in the presence of traces of substances known to inhibit the glow of phosphorus.

Working on this problem, I find that the intermittent luminosity and formation and propagation of luminous pulses could be obtained equally strikingly in an open vessel containing air, such as a test tube, flask, or tube open at both ends, if traces of these inhibitors—*e.g.*, naphthalene, carbon disulphide, turpentine, light petroleum—are present. The effect is particularly good if the vessels be wet with water. No intermittence or pulse-formation is observed with water alone. It is also found that the luminous pulses *creep along the surface* of the vessels.

It is well-known that the luminosity of phosphorus is inhibited in pure oxygen above a critical pressure (depending on the temperature), and that it becomes intermittent near the critical pressure.

The explanations offered for the periodic nature of the glow and its propagation in the presence of water and inhibitors (Rayleigh, *loc. cit.*; Joubert, *Ecole. Norm. Annales*, 1874, III., 209; Jorissen, *Chem. Weekblad*, 1918, XV., 705) have all been based on the view that here we are dealing with the propagation of combustion in an explosive mixture. The fact that exactly similar effects are produced, even in open vessels containing excess of air, and the clearly creeping nature of the propagation of the glow necessitate a modification of this view. It appears probable that the effect in oxygen at the critical pressure of inhibition and that

observed in the presence of the "inhibitors" are both due to similar causes.

The luminosity of phosphorus, its inhibition, intermittent nature in presence of "inhibitors" and the formation and nature of propagation of the luminous pulses could all be strikingly shown as a lecture experiment by the following simple arrangement.

A very dilute solution of phosphorus in carbon disulphide is prepared and poured over a long narrow strip of filter paper or a cotton thread, suspended from an open glass tube inserted in a cork. The solvent is allowed to evaporate almost completely, so that fumes begin to appear on the strip. The cork is then loosely inserted into a conical flask of height greater than the length of the strip. Luminous pulses are seen to form and travel up and down along the strip. The formation of the pulses alternate with dark intervals. In the later stages the pulses travel along the sides of the flask also. If the strip happen to be permanently bright, a trace of carbon disulphide vapour introduced into the flask will start the above phenomena.

*Chemistry Laboratory,  
H.H. The Maha Rajah's College,  
Trivandrum.*

## THE MECHANISM UNDERLYING THE REACTION BETWEEN ETHYL CYANOACETATE AND TAUTOMERIC SUBSTANCES OF THE KETO-ENOL TYPE.

By R. F. HUNTER, F.C.S.

The condensation of ethyl cyanoacetate with ketones has been the subject of many investigations. In this paper, however, we are only concerned with the recent work of Dr. C. K. Ingold, which was carried out at the Royal College of Science a year or two ago. Usually the first product which can be isolated is an unsaturated cyano ester, in which the double bond is situated either in the  $\alpha\beta$  or  $\beta\gamma$  position in respect to the carboxyl group. For instance, acetone yields the  $\alpha\beta$  unsaturated condensation product, whilst cyclohexanone gives mainly a cyano ester in which the double bond occupies the  $\beta\gamma$  position. The latter type of reaction appears to be the one most frequently met with, and it is possible to ascribe the production of cyano methylcrotonic ester from acetone to the instability of the unsaturated isomeride that is intermediate in



of work, dismissals of workmen, low wages and high prices which exceed the world's market level more and more, are characteristic of the low condition of economic life.

#### *Mining.*

The Upper Silesian pit-coal production was normal during the first three weeks of the month. On October 22 a strike broke out, and gradually extended to all mines, but work was reported to have been resumed on October 30.

In Central Germany conditions in the brown coal and potash mines were unfavourable. In all districts lack of sales was complained of. The curtailment of working hours, the dropping of shifts, dismissals, and the closing of one mine became necessary. Up to three shifts a week were dropped. In the Mansfeld copper schist mines the position became so bad that two shifts had to be dropped.

In the Berlin coal trade the introduction of gold mark invoicing caused great difficulties. Payments were considerably delayed. Delays occurred not only in local trade, but also, in particular, in the industry which, owing to declining employment and increased paper mark prices, was unable to effect prompt payment. On the other hand, the pits press more and more for speedy payment in order that they may be ready to meet wage demands which increase almost daily.

Inland business in the Halberstadt potash industry was almost completely stagnant, in spite of the fact that prices were reduced during the course of the month. Foreign trade was better, but still quiet.

In the iron ore industry in the Siegesland and Dill districts, further mines were compelled to close down or to restrict operations considerably. Conditions in the mines where the work is exclusively underground were particularly unfavourable, as they had to bear the full cost of pumping the water even where the mines had been closed down.

#### *Iron, Machinery, and Electro-Technical Industries.*

The abandonment of passive resistance did not change the position in the Ruhr. As before, the pits and foundries were idle. Their position could scarcely be imagined more intolerable. Coal and coke supplies continued to be despatched by the French. The supplies of bye-products, such as ammonia, benzole, coal-tar, resin, raw naph-

thaline, etc., were completely cleared by the French.

In Upper Silesia, employment in the Opeln pig iron and finished products works was still satisfactory. Orders, however, declined during the course of the month. Foreign trade was completely stagnant.

The electro-technical industry reported that prices for semi-manufactures were high and delivery periods short. The market is small and stagnant. Individual works report falling prices. Short-time work has been introduced on a fairly large scale.

#### *Chemical Industry.*

The business position was such that more workers had to be dismissed, and presumably a further restriction of operations is to be reckoned with in the Wiesbaden district.

#### *India-Rubber Industry.*

There was no improvement in the position of the Hanover india-rubber industry. The market possibilities at home have grown worse, so that a curtailment of working hours and further dismissals of workmen could not be avoided.

#### *Timber Industry.*

In the saw-mills and in the wood trade business was almost at a standstill. Only small transactions were concluded which served to fill up stocks. Business with England appeared to experience a slight revival.

#### *Clothing Industry.*

In the wool wholesale trade business, as before, could not be revived, as, owing to the large amount of unemployment in the textile industry, the demand remained very small. Wool prices were firm, and there was the less anticipation of a fall, as, in view of the fact that the wool shears have yielded only a small quantity of fine wool, an increased demand will be met by a small supply. Conditions also grew worse in the carded yarn spinning-mills. In occupied territory the demand was extremely small owing to the position of the cloth industry. Deliveries to districts on the right bank of the Rhine were out of the question, in view of the difficulties of transport and, above all, to the fact that the costs of production had far exceeded the world's market price.

In the Aix-la-Chapelle cloth industry, the stock of orders was extremely small. Practically no new orders were received. Foreign business was also almost at a standstill. The high costs of production have greatly impaired the power to compete on the

foreign market. In the cloth trade business was irregular, and was, in general, confined within narrow limits.

#### Leather Industry.

The prices for raw hides and skins of all kinds rose continually, both at the auctions and on the open market. A much larger turnover would have been obtained had not the dearth of money made itself exceptionally felt.

#### MEDICAL SUPPLIES FOR THE DUTCH GOVERNMENT.

Mr. R. V. Laming, O.B.E., H.M. Commercial Secretary at The Hague, reports that the Dutch Government are calling for tenders, to be presented by November 27, for the supply of various medical supplies.

Applications from United Kingdom firms for further particulars should be addressed to the Department of Overseas Trade (Room 52), 35, Old Queen Street, London, S.W.1. (Reference No. 30953/F.W./C.C./ (2).

#### REPORT ON THE CONSUMPTION OF PREPARED NON-METALLIC MINERALS IN CANADA.

An investigation has been made to determine the extent of the market in Canada for finely-ground non-metallic minerals, and this report on the consumption of certain non-metallic minerals in Canada has been prepared with a view to exploring the possibility of establishing plants in Canada for the production of finely-ground non-metallic commodities for home consumption. The consumption of these commodities in Canada is considerable in the aggregate, and comprises many different varieties. Heretofore, though extensive deposits of the crude material are known to exist in Canada and though these deposits are in certain cases being worked, the bulk of the supply has been derived from importations.

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL SOCIETY.

THURSDAY, NOVEMBER 15.

Papers read:—

SIR WILLIAM BRAGG, F.R.S., and PROF. G. T. MORGAN, F.R.S.: *Crystal Structure and Chemical Constitution of Basic Beryllium Acetate and Propionate.*

Basic beryllium acetate is shown by X-ray analysis to be a highly co-ordinated compound. The molecule is a perfect tetrahedron, having an oxygen at the centre, a beryllium alone at each corner and an acetyl group associated with each edge. The crystalline structure is the same as that of diamond. The propionate forms a monoclinic crystal. The propyl group can no longer be arranged so as to possess a plane of symmetry, as in the case of the acetyl; and in consequence the symmetry is much less.

L. C. JACKSON: *Investigations on Paramagnetism at Low Temperatures.* Communicated by Prof. H. Kamerlingh Onnes, For. Mem. R.S.

G. I. TAYLOR, F.R.S.: *Experiments on the Motion of Solid Bodies in Rotating Fluids.*

Part I. Powdered substances. The following paramagnetic substances have been investigated from atmospheric temperature down to lowest temperature obtainable with liquid hydrogen (about 14° K.): anhydrous sulphates, heptahydrated sulphates and ammonium double sulphates of cobalt, nickel and ferrous iron. New phenomena of considerable interest have been found at the lowest temperatures. Thus, whilst these substances follow the Weiss law  $\chi(T + \Delta) = C$  at relatively high temperatures, the following types of deviation from this law were found at the lowest temperatures: (1) Susceptibility increases more rapidly with fall in temperature than is given by Weiss law. (2) The curve of  $\frac{1}{\chi}$  against  $T$  pos-

sesses a point of inflection. (3) A maximum and a minimum value of susceptibility occur in region of lowest temperatures.

Part II. Crystals. The principal sus-

ceptibilities of crystals of cobalt ammonium sulphate and nickel sulphate (heptahydrate) have been determined over a temperature range of 290° K. down to 14° K. These are the only data yet available as regards the principal susceptibilities of crystals at very low temperatures. In both cases each of the principal susceptibilities follows the Weiss law at higher temperatures, but deviates therefrom at lower temperatures. The Curie constant  $C$  is same for each of principal susceptibilities of any crystal. Deviations from Weiss law in cases of cobalt ammonium sulphate fall into category (1) above, while those of nickel sulphate fall into category (2).

An attempt is made to connect magnetic phenomena with the structure of crystals.

L. C. JACKSON and PROF. H. KAMERLINGH ONNES, FOR. MEM. R.S.: *The Magnetic Properties of some Paramagnetic Double Sulphates at Low Temperatures.*

In continuation of a previous investigation the magnetic susceptibilities of the following powdered substances have been measured over a range of temperature of from atmospheric temperature down to about 14° K.: cobalt potassium sulphate, cobalt rubidium sulphate, manganese ammonium sulphate. The results of the two cobalt compounds show that these substances follow the law  $\chi(T+\Delta) = \text{const.}$  at not too low temperatures, but deviate therefrom at the lowest temperatures, in such a way that susceptibility is *greater* than value calculated from the above law, thus confirming the results previously obtained with cobalt ammonium sulphate.

Contrary to first expectation, it was found that the  $\Delta$ 's of the three above-mentioned cobalt compounds were nearly equal. It is shown, however, that this result is indeed to be expected by a consideration of data already published for the principal susceptibilities of cobalt ammonium sulphate and the conclusions drawn by Tutton as to the structures of these monoclinic double sulphates from his well-known crystallographic investigations.

Manganese ammonium sulphate was found to obey the Curie law,  $\chi T = \text{const.}$ , down to the lowest temperature investigated. This result fits well with the known behaviour of other manganese salts, showing that in this series of compounds the substance follows Curie's law more closely the greater its "magnetic dilution."

H. H. POTTER: *Some Experiments on the Proportionality of Mass and Weight.* Communicated by Prof. O. W. Richardson, F.R.S.

The gravitational accelerations of lead, steel, ammonium fluoride, bismuth, paraffin wax, duralumin and mahogany have been compared with that of brass, and no difference greater than that attributable to experimental error has been found. An accuracy of one part in 50,000 has been obtained. Special attention has been given to two substances, ammonium fluoride and paraffin wax, which have large hydrogen contents.

Papers read in title only:—

LORD RAYLEIGH, F.R.S.: *Further Studies on the Glow of Phosphorus and its Extinction by Moist Oxygen.*

The velocity of blast necessary to blow away the glow of phosphorus increases enormously with rise of temperature. On the other hand, it is enormously diminished by enriching the air blast with oxygen. In either case the range examined was of order 1,000 times. This velocity of blast measures rate of propagation upstream of glow through mixture of phosphorus vapour and oxygen.

Where velocity is reduced, by cooling or by adding oxygen, to less than 1 cm./sec., the condition of extinction is approached. From this viewpoint the known extinction by moist oxygen alone is seen to be the limiting case of slow propagation. It follows that extinction is due to failure of the process causing propagation. This was shown before to be in all probability a catalytic action of products of combustion. Excess oxygen, like other inhibiting substances, "poisons" these products or makes them unfit to act—perhaps by a process of condensation, similar to that which is found to clog the motions of ions in gaseous combustion.

PROF. H. A. WILSON, F.R.S.: *An Experiment on the Origin of the Earth's Magnetic Field.*

H. ROBINSON, D.Sc.: *The Secondary Corpuscular Rays produced by Homogeneous X-Rays.* Communicated by Sir Ernest Rutherford, F.R.S.

The original Robinson-Rawlinson method of investigating velocities of secondary cathode rays produced by X-rays has been developed with a view to increased accuracy. Special attention has been paid to homo-

generality of the primary X-ray beam, and the effect of fluorescent radiations of the material under investigation has been thereby reduced.

The velocities of secondary electrons are measured by deflection in the magnetic field on a pair of large Helmholtz coils. The copper,  $K\alpha$ , rays are used as primary X radiation. This choice permits of measurements being made in regions already mapped out by X-ray spectroscopy, and also allows some of the less known parts of the spectrum to be investigated. Satisfactory agreement with existing data has been found in the former region.

It has been possible to separate and measure five of the N absorption edges of bismuth, the remaining two not being separated from the O rings. All five M edges have been measured for atoms as light as tungsten. The L limits have been measured as far as copper, and the K limits to oxygen. The very soft limits cannot at present be measured very accurately, but reasons are given for believing that K limits of light atoms may be higher than accepted values.

Intensities of lines of corpuscular spectra are estimated and discussed. Progressive changes are found to occur along the series of elements in relative intensities of different members of the same group.

LT.-COL. J. W. GIFFORD (with an Introduction by PROF. T. M. LOWRY, F.R.S.): *Some Refractive Indices of Benzene and Cyclohexane*. Communicated by Prof. T. M. Lowry, F.R.S.

J. A. V. BUTLER: *A Note on "The Significance of the Electrode Potential."* Communicated by Prof. J. W. McBain, F.R.S.

1.—A thermodynamical argument given in Heyrovsky's paper on The Significance of the Electrode Potential is examined, and it is shown that certain stages of the cyclic process employed are irreversible and that the conclusions are therefore erroneous.

2.—A method of conducting the cyclic process reversibly is given, and it is shown that the sum of the differences of potential round the cycle is zero; it follows that no information regarding the relations between the electrode potentials and the various chemical equilibrium constants is obtained by the use of a cyclic process of this kind.

## THE ROYAL SOCIETY.

THURSDAY, NOVEMBER 22.

Papers read:—

F. SIMEON: *The Carbon Arc Spectrum in the Extreme Ultra-violet. II.* Communicated by Prof. A. W. Porter, F.R.S.

H. J. GOUGH and D. HANSON, D.Sc.: *The Behaviour of Metals subjected to Repeated Stresses.* Communicated by Sir Joseph Petavel, F.R.S.

W. SUCKSMITH and L. F. BATES: *On a Null Method of Measuring the Gyro-Magnetic Ratio.* Communicated by Prof. A. P. Chattock, F.R.S.

J. H. SHANBY: *Studies in Brownian Movement, II. The Determination of Avogadro's Number from Observations on Bacteria (Cocci).* Communicated by Prof. S. W. J. Smith, F.R.S.

Papers read in title only:—

H. HARTRIDGE, Sc.D., and F. J. W. ROUGHTON: *The Kinetics of Haemoglobin, II.* Communicated by Prof. J. N. Langley, F.R.S.

A. F. A. YOUNG: *The Thermionic and Photo-Electric Properties of the Electro-Positive Metals.* Communicated by Prof. O. W. Richardson, F.R.S.

O. F. T. ROBERTS: *The Theoretical Scattering of Smoke in a Turbulent Atmosphere.* Communicated by Dr. G. C. Simpson, F.R.S.

## ROYAL INSTITUTION.

The 98th Course of Juvenile Lectures at the Royal Institution to be delivered this Christmas by SIR WILLIAM BRAGG, F.R.S., is entitled *Concerning the Nature of Things*, and will deal with I., *The Atoms of which Things are Made*; II., *The Nature of Gases*; III., *The Nature of Liquids*; IV., V., and VI., *The Nature of Crystals*, (a) *Diamond*, (b) *Ice and Snow*, (c) *Metals*.

The first lecture will be given on Thursday, Dec. 27, 1923, and the succeeding ones on Dec. 29, 1923, and Jan. 1, 3, 5, and 8, 1924.

## THE CHEMICAL SOCIETY.

Papers read at the Ordinary Scientific Meeting, November 15:—

*Ring-chain Tautomerism. Dynamical Evidence Relating to the Mutarotation of the Sugars*, by J. W. BAKER, C. K. INGOLD, and J. F. THORPE.

An earlier paper on the mechanism of mutarotation, dealing not only with dynamical, but also with structural and other aspects of the problem, showed that the mutarotation-time curves have (a) a form; (b) a spacing, on the mutarotation-time-concentration diagram, which are entirely at variance with the dynamical consequences of the intermediate-hydrate theory, but are in complete agreement with the hypothesis of ring-chain tautomerism, to which structural evidence also points. It has been objected that the derivation of the dynamical consequences of the hydrate theory was based on a fallacy. The authors do not accept this, and now present the complete mathematical analysis on which their conclusions were based.

*An X-Ray Investigation of certain Organic Esters, and other Long Chain Compounds*, by G. SHEARER.

By means of an accurate X-ray reflexion method, measurements have been made upon solid crystalline films of methyl, ethyl, octyl, and cetyl palmitates, of methyl and ethyl stearates, of *p*-hexadecylphenol, *p*-octadecylphenol, and of octadecylbenzene. As in Müller's experiments on normal fatty acids, very good reflexions were obtained from what are probably the crystal cleavage-planes, the distances or "spacings" between which can thus be determined. The cleavage spacings of the palmitic esters increase regularly with the number of carbon atoms in the alkyl group; and the increment per carbon atom of the chemical formula is the same for these esters as for the two stearates studied, namely, 1.22 A.U. for each  $\text{CH}_2$  of the alkyl radicle. When the palmitic and stearic esters of a given alkyl radicle are compared, the increment in spacing per  $\text{CH}_2$  of the acid radicle is found to be 1.0. This figure agrees with Müller's value of 2.0 in the case of the free fatty acids, if his assumption is adopted that there are two molecules end-to-end between the cleavage planes of the free acids, and if only one be allowed in the cell of the esters. The accepted and independently measured

"diameter" of the carbon atom is 1.5 A.U. In order that chains, built of atoms of this diameter, shall have the perpendicular distance of 1.22 A.U. between contiguous carbon atoms, which is shown to prevail in the alkyl chains, it is necessary, either that the chains shall be tilted at an angle to the cleavage planes, or else, if their lengths are perpendicular to the planes, that the carbon atoms should be linked spirally or zig-zag. It is possible to calculate the observed cleavage spacings from the molecular formulae, placing one or else two molecules between successive cleavage planes as already indicated, by using the independently-known "atomic radii," and by allowing that an acid radicle increases by 1.0 A.U., an alkyl radicle by 1.22 A.U., per  $\text{CH}_2$  group; where necessary, W. H. Bragg's value for the dimensions of the benzene ring is also used.

*Further X-Ray Measurements of Long Chain Compounds, and a Note on their Interpretation*, by ALEX. MULLER and G. SHEARER.

Data were given for the cleavage spacings of undecylic, pentadecylic, and margaric acids; for oleic, elaidic, and *iso*-oleic acids; and for erucic and brassidic acids.

A systematic exposition was given of the conclusions which can legitimately be drawn from these experiments. In the case of stereoisomers of a given unsaturated acid, the observed differences, when expressed in terms of the two types of chain, lead to the inference of *cis-trans* isomerism, and point to a definite attribution of structure as between the two isomers. The differences between corresponding saturated and unsaturated "straight-chain" acids were discussed.

*The Constitution of the Disaccharides. Part IX.: Gentiobiose. Its identity with Amygdalin Biase*, by W. N. HAWORTH and B. WYLAM.

On hydrolysis of completely methylated gentiobiose, 2,3,5,6-tetramethylglucose and 2,3,5-trimethylglucose were obtained. Gentiobiose thus possesses the same constitution as both maltose and amygdalin biase, and since the latter sugar contains a  $\beta$ -linking uniting the two glucose residues exactly as does gentiobiose, this is the disaccharide which occurs in amygdalin. Synthetic work also confirmed this result.

*The Constitution of Raffinose*, by W. N. HAWORTH, E. L. HIRST and D. A. RUELL.

Raffinose, prepared from cotton seed meal, gave rise on methylation to hendecamethyl raffinose, b.p. 238° C. /0.02 mm.,  $[\alpha]_d = +128^\circ$ . Hydrolysis with 1 per cent. hydrochloric acid led to the isolation of three partly methylated hexoses, tetramethyl  $\gamma$ -fructose identical with that isolated from methylated sucrose, 2,3,5-trimethyl glucose (butylene oxidic), which gave a crystalline methylglucoside melting at 94° C., and a tetramethyl galactose, which gave a crystalline anilide identical with that prepared from methylated lactose. A structural formula was raffinose was deduced.

It appears that the constitution of melibiose is to be represented by a formula in which the glucose unit, through the hydroxyl group attached to its terminal carbon atom 6, is linked with the reducing group of galactose.

#### THE FARADAY SOCIETY.

(Concluded from last week.)

Papers read at the meeting on November 12:—

*The Effect of Sucrose on the Rate of Coagulation of a Colloid by an Electrolyte*, by LEONARD ANDERSON, PH.D.

The concept that the activity of ions, rather than their concentration, was likely to play an important part in chemical kinetics was first suggested by Harned. The interesting problem arises as to whether the activity of the added electrolyte ions does or does not play the significant roll in a typical colloidal phenomenon, namely the rate of coagulation of a colloid in presence of added electrolyte.

The work of Moran and of Corran has shown that sucrose possesses the property of causing a large increase in the activity of various ions whilst not appreciably altering their concentration. It was, therefore, considered of interest to investigate the influence of sucrose on the coagulation of a typical colloid, gold hydrosol. In colloid systems the Smoluchowski<sup>1</sup> equation is the only one, possessing a strictly theoretical

basis, which deals with the kinetics of coagulation. From the work of Anderson and of other investigators,<sup>2</sup> however, this equation appears to be limited to rapid coagulation. In the present instance, a slow or moderately rapid rate of coagulation was considered best, since, in this region, the rate of coagulation is very sensitive to slight variations in the concentration of the coagulant. In view of the inapplicability of the Smoluchowski equation to this region, a more arbitrary method of measuring the rate of coagulation was chosen, namely, the time required for the originally red gold sol to reach the tint of a partially coagulated gold sol, stabilised by addition of gelatin.

From the literature it appears to be uncertain whether sucrose does or does not behave as a peptiser towards colloidal sols. Bancroft enumerates certain cases in which sucrose does peptise. Chatterji and Dhar, however, state that true peptisation by sucrose is doubtful. The addition of sucrose to the colloid system increases the viscosity and should thereby lower the speed of coagulation. The sucrose, however, besides affecting the mobility of the colloidal particles also affects the mobility of the coagulating ions.

The experiments indicated that the sucrose had a two-fold action. The first was a definite peptising effect, and the second an accelerating effect, upon the coagulation of colloidal gold by certain electrolytes. In the case of potassium chloride as electrolyte the peptising action was most marked and rapidly increased as the sucrose increased. In the case of barium chloride, in presence of sucrose, the coagulation proceeded more rapidly (above 10 per cent. sucrose) than it should do on the basis that activity is the sole factor determining the rate of coagulation. From this it would appear that the sucrose, in addition to its peptising effect, also introduced a specific augmentation of coagulation in excess of what would be anticipated. The latter effect is apparently least in the case of potassium chloride and greatest in the case of barium chloride. In

<sup>1</sup> Smoluchowski, *Zeitschr. physikal. Chem.*, XCII., 129, 1917.

<sup>2</sup> Anderson (*Trans. Faraday Soc.*). Kruyt and Arkel, *Rec. Trav. Chim. Pays-Bas.*, XXXIX., 656, 1920. Westgren and Reitstotter, *Zeitschr. physikal. Chem.*, XCII., 750, 1917. Mukherjee and Papaconstantinou, *Phil. Mag.*, XLIV., 305, 1922.



the case of hydrogen ion the value of  $\frac{T}{\eta}$  is

constant above 10 per cent. sucrose which may indicate that the peptising effect of the sucrose was just counterbalanced by the specific augmenting effect and consequently in the case of HCl the true activity apparently showed itself.

Sucrose of itself had no apparent coagulating power on gold sol. As regards the augmentation of the coagulating efficiency of ions produced by the sucrose it might be suggested that possibly the effect was due to the alteration in the dielectric capacity of the medium as a result of the increase in the sugar content. Measurements of the dielectric capacity of sugar solutions indicated a marked fall as compared with that of water. The electrical adsorption of the ions would therefore be intensified, involving an increase in neutralising efficiency on the electrical charge of the colloid particles, with a consequent increase in the rate of effective collisions, i.e., effective in respect of coagulation, on the part of the colloid particles. If this is the case the horizontal line obtained in the case of hydrogen ion was largely accidental, and the results can only be regarded as qualitative evidence in favour of the activity of ions as a significant factor for coagulation.

It was established from the experimental evidence that in the coagulation of gold sols by hydrochloric acid, barium chloride and potassium chloride in presence of varying amounts of sucrose at 25° C, when the concentration of the hydrogen ion was maintained constant, the time of coagulation, corrected for viscosity, was found to pass through a maximum at about 10 per cent. sucrose.

When the activity of the H ion was maintained constant, the time of coagulation corrected for viscosity rose until 10 per cent. sucrose was reached and then became constant.

In the case of barium chloride, the same conditions were observed, and in both cases

the value of  $\frac{T}{\eta}$  passed through a maximum

at about 10 per cent. sucrose.

In the case of potassium chloride the concentration of the potassium ion was maintained constant. It was found, contrary to

anticipation, that  $\frac{T}{\eta}$  increased continu-

ously as the sucrose content increased.

Sucrose exerts a definite peptising effect upon colloidal gold, and it also exerts a specific augmentation of coagulation in the case of hydrogen and barium ions over and above that of increasing the activity of these two ions. It is thus evident that sucrose is by no means inert towards ions and gold sols. It exhibits apparent antagonistic action.

The experiments indicated in general, however, that the coagulating power of an ion is dependent upon its activity rather than upon its concentration, a conclusion which brings the typical colloid phenomenon of coagulation into line with the kinetics of chemical change in homogenous (molecular) systems.

*A Method of Measuring the Rate of Coagulation of Colloidal Solutions over Wide Ranges*, by H. H. PAINE, M.A., B.Sc., and G. T. R. EVANS, B.Sc., University of the Witwatersrand, Johannesburg.

Considerable light was thrown on the kinetics of coagulation some few years ago in papers by Smoluchowski, and by Freundlich. These writers considered a colloidal solution from the point of view of the kinetic theory. Coagulation is regarded as the "coalescence" of "molecular" particles resulting from their mutual collision.

Smoluchowski was concerned primarily with coagulation when it occurs at its maximum rate—that is, when all collisions between colloidal particles result in coalescence. The existence of this maximum is demonstrated by Zsigmondy with gold sol, and by Kruyt and van Arkel with selenium sol. When successive samples of the colloidal solution were treated with increasing amounts of an electrolyte, the rates of coagulation increased to a maximum or limiting value.

Freundlich extended the theory to slow coagulations, and made a further inquiry into the forces between the particles. His theory states that in the case of a stable colloidal solution, the collisions between particles are "elastic," i.e., they do not result in coalescence. A repulsion (something which prevents coalescence) exists between two particles arising from the existence of the electrical double layer. As soon as the potential difference across this double

layer is reduced beyond a certain critical value, the repelling force vanishes, and a collision results in coalescence. This critical point has, then, many of the properties originally assigned to the isoelectric point.

It occurred to us that the work could be extended by the use of a "protective colloid." The addition of gelatine or starch results in making the colloid less sensitive to electrolytes, *e.g.*, Luers showed that the time taken for a change to be observed in a Congo ruby sol on the addition of an electrolyte is increased if gelatine is present.

Coagulations which normally proceed rapidly, can be retarded until the methods for studying relatively slow coagulations can be applied. We have observed coagulation proceeding at its "limiting rate" for a colloidal copper solution to which a suitable quantity of starch had been added.

The rate of coagulation of colloidal copper solutions was studied for a wide range of electrolyte concentrations by making use of the retarding effect of starch. Very rapid coagulations can thus be brought into the region of observation by ordinary methods. A "Transformation Factor" can be obtained which enables us to calculate what the rate of coagulation would have been for the pure colloid.

The results of these experiments agree closely with the equation deduced by Freundlich for the variation of the rate of coagulation with the concentration of the electrolyte. In particular, they confirm the existence of a maximum rate of coagulation.

Concentrations of starch below a certain minimum do not influence the rate of coagulation. If we express this influence by the "transformation factors," a linear relation holds between the logarithm of the transformation factor and the concentration of the starch over and above some minimum value.

*Studies in Heterogeneous Equilibria.*—Part I.: *Conditions at the Boundary Surface of Crystalline Solids and Liquids, and the Application of Statistical Mechanics*, by J. A. V. BUTLER, M.Sc.

Equilibrium between two phases occurs kinetically when equal numbers of molecules of every species concerned pass the boundary surface in both directions in the same time. The methods of statistical mechanics have been applied to the development of the kinetics of such processes only in the simplest cases.

Langmuir, whose pioneer work has inspired most of the recent progress in this direction, was concerned with vaporisation and the kinetics of gas reactions at solid surfaces. Rideal and Rodebush have employed special forms of the statistical equations with some success in the calculation of the constants of vaporisation. Langmuir's treatment has been extended to give a kinetic theory of the adsorption of gases by Henry. A tentative attempt to apply statistical equations to the calculation of solubility is mentioned by Dushman.

The subject is here approached from a somewhat different point of view, which may perhaps be made clearer by analogy. In the study of homogeneous equilibrium the law of mass action proved a reliable guide and inspiration for many years, although it gave merely the form of the equilibrium equation and did not lead to the calculation of the equilibrium constant in any case. The earlier workers on heterogeneous equilibrium approached the subject from the point of view of the law of mass action, but the results were comparatively meagre. Certain analogies with mass action obviously exist, but the backward state of our knowledge of the kinetics of phase equilibria may be traced to the fact that no general kinetic law of surface action has been available to replace the law of mass action.

The author showed that although it is not yet possible by the application of statistical methods to calculate the values of the equilibrium constants, nevertheless these methods can be used to co-ordinate diverse cases of heterogeneous equilibrium, in particular solubility, the solubility product, the electromotive equilibria of metals and oxidation potentials.

Although this treatment does not aim primarily at the calculation of equilibrium constants and may have a very distinct usefulness if it is at present unable to achieve that objective, it is evident that every opportunity should be taken of making a comparison with numerical data. In these complex cases the exact calculation of equilibrium constants is only likely to be achieved when the special conditions of each case have been qualitatively explored.

The present paper was devoted to a preliminary discussion of the conditions at the boundary surfaces between crystalline solids and liquids from this standpoint and the deduction of appropriate statistical conditions.

The extension of the methods to the spe-

cial case of metals dipping into their salt solutions, taking into account the electric factors concerned, have led to a physical interpretation of Nernst's electrolytic solution tension. A further extension provided a reasonable explanation of the mechanism whereby reversible oxidation potentials are set up at inert electrodes.

### THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

Paper read at the Royal Society of Arts on Tuesday, November 13:—

*Galician-Canadian Pole Tool Fishing Methods*, by ALBERT MILLAR, A.M.I.-MECH.E. (Member).

"Fishing" in oil well nomenclature covers a great variety of work, and does not merely represent the recovery of lost tools as is often thought to be the case. Side-tracking of tools or casing also come under the heading of "Fishing."

In all these operations "touch" plays a most important part, and this sense can only be acquired by long practice, as can also the knack of constructing suitable fishing tools to suit individual cases.

The author dealt very exhaustively with all the aspects of the problems involved in recovering lost tools, and in dislodging those that became stuck. The methods to be adopted, it was pointed out, differed according to the circumstances, from the case of slightly bent tools to a troublesome accident due to runaway tools or casing.

### THE INSTITUTION OF ELECTRICAL ENGINEERS.

A joint meeting with the Societe des Ingenieurs Civils de France (British Section) was held on Thursday, November 22. A paper entitled *The Electrification of the Midi Railway* was read by MONSIEUR A. BACHELLERY.

The Wireless Section held a meeting on Wednesday, November 21. Papers entitled *Periodic Trigger Reception*, by Mr. E. V. APPLETON, M.A., D.Sc., and F. S. THOMPSON, B.A. (Royal Corps of Signals), and *A Dynamic Model of a Valve and Oscillating Circuit*, by Mr. R. C. CLINKER, M.I.E.E., were read.

The joint meeting with the Societe des Ingenieurs Civils de France (British Section), which was to have been held on Thursday, November 15, was postponed to Thursday, November 22, at 6 p.m., when MONSIEUR A. BACHELLERY read his paper on *The Electrification of the Midi Railway*.

JOINT MEETING WITH THE PHYSICAL SOCIETY OF LONDON, THURSDAY, NOVEMBER 29, 1923.

The above meeting will begin at 5.30 p.m. (light refreshments at 5 p.m.), and will be in two sessions, viz.: 5.30 to 7 p.m., and 8 to 9.30 p.m.

The subject to be discussed will be: *Loud Speakers for Wireless and other Purposes*, and among those who will contribute short papers (including in some cases practical demonstrations) will be the following:—

Mr. S. G. Brown, F.R.S.; Captain P. P. Eckersley; Professor, C. L. Fortescue, M.A.; Professor J. T. MacGregor-Morris; Professor E. Mallett, M.Sc. (Eng.); Mr. L. C. Pocock, B.Sc.; Mr. H. L. Porter, B.Sc.; Professor A. O. Rankine, D.Sc., F.R.S.; Mr. E. K. Sandeman, B.Sc.; Mr. G. A. Sutherland, M.A.

By kind permission of the British Broadcasting Company arrangements are being made for parties, limited to 20 in number, to visit the Company's studio at No. 2, Savoy Hill, at half-hourly intervals from 3 to 5 p.m. Members wishing to visit the studio are requested to send their names to the Secretary, and to indicate the time which would be most convenient to them.

### THE ROYAL AGRICULTURAL SOCIETY OF ENGLAND.

The proceedings at the Monthly Council, held on November 7, Lieut.-Col. E. W. Stanyforth (President) in the chair, included the presentation of various reports. The following is the chemical report:—

Mr. J. L. Luddington (Chairman) reported that a letter had been received from the Departmental Committee on the Fertilisers and Feeding Stuffs Act, inviting evidence from the Society. Arrangements had been made for the Chairman to give evidence on behalf of the Society. Several points arising on a memorandum received from the Ministry of Agriculture had been considered by the Committee, who had instructed their representative as to the action to be taken thereon.

The Committee recommended that a re-

port by the Consulting Chemist, including the names of the vendors of the materials mentioned, be published as a private and confidential document to Governors and Members.

A draft of a proposed new by-law defining the duties of the Committee had been read and approved.

### THE ROYAL MICROSCOPICAL SOCIETY.

*President:* Professor Frederic J. Cheshire, C.B.E., F.Inst.P.

*Hon. Secretaries:* Joseph E. Barnard, F.Inst.P., James A. Murray, M.D.

A meeting of the Society was held on November 21. The following papers were read and discussed:—

*Sex-Reversal and Intersexuality*, by Mr. F. ROGERS BRAMBELL, B.A., B.Sc.

*Further Evidence on the Transition of Peritoneal Cells into Germ-Cells in Amphibia*, by PROF. J. BRONTE GATENBY, M.A., D.Ph., M.R.I.A., F.R.M.S.

*The Preparation of Eel Scales for Microscopic Examination*, by DR. MILES JOHNSTON, M.B., CH.B.

*The Microscope in Physics*, by MR. F. I. G. RAWLINS, M.R.I., F.R.M.S.

DR. H. M. WOODCOCK (Lister Institute of Preventive Medicine) exhibited Bacteriomorphic Granules (or Granules simulating Bacteria) resulting from Cell-lysis or Digestion.

The section of the Royal Microscopical Society formed to deal with the Industrial Applications of the Microscope, and to assist in the development of Industrial Research in British Industries, will hold its next meeting at 20, Hanover Square, W.1, on Wednesday, November 28, 1923, at 6.30. The following exhibits have been arranged:

Mr. Conrad Beck, C.B.E., F.R.M.S.: A New Projection Microscope for measuring

Fine Wires and Fabrics to  $\frac{1}{50000}$  inch.

Messrs. Adam Hilger, Ltd.: Dr. Müller's

X-Ray Spectrograph for the Examination of Sub-Microscopic Crystalline Structures.

Mr. J. E. Barnard, F.Inst.P., F.R.M.S., will give a Lecture Demonstration: The characteristics of a microscope for general and special purposes; the tests for mechanical efficiency that should be satisfied.

DR. SIDNEY H. BROWNING, L.R.C.P., M.R.C.S., F.R.M.S., will read a paper entitled *The Application of the Microscope to Industrial Diseases*.

MR. CHARLES A. NEWTON, F.R.M.S., will also read a paper entitled *The Microscope in the Examination of Condensed Milk*.

### THE SOCIETY OF GLASS TECHNOLOGY.

A meeting of the Society of Glass Technology was held in the Lecture Room of the Department of Coal Gas and Fuel Industries, The University, Leeds, on Wednesday, November 21.

The following papers were received and discussed:—

*Note on the Influence of Rapid Chilling on the Reversible Expansion of Clay*, by H. S. HOULDSWORTH, M.Sc.

*Glasshouse Pots: Some Notes on their Manufacture and Use*, by P. MARSON.

*The Casting Process for Glasshouse Refractories in German Glass Plants*, by PROF. KURD ENDELL, DR. PHIL.

By the courtesy of the Directors and of H. J. C. Johnstone, Esq. (General Manager), a visit was made to the Wortley works of Messrs. Leeds Fireclay Co., Ltd., Wortley, Leeds, on November 21. At these works members had an opportunity of inspecting pot clay blocks, firebricks, blast furnace linings, coke oven bricks, and drain pipes.

### THE MINERALOGICAL SOCIETY.

ANNIVERSARY MEETING, NOVEMBER 6.

Dr. A. Hutchinson, F.R.S., President, in the chair.

Papers read:—

DR. L. J. SPENCER, *Eucrase and Platinum from Diamond-washings in British Guiana.*

Small discs resembling fossil corals consist of a radial aggregation of euclase crystals so arranged that the plane of symmetry is always parallel to the surface of the disc. These, together with tourmaline, diamond, gold, and platinum, were found in the conglomerates near the Kaieteur Falls on the Potaro River. Platinum has not hitherto been recorded from British Guiana.

HAROLD E. BUCKLEY, *Some Anomalous Optical Properties of Freshly-prepared mixed Crystals of the Seignette Salts.*

In the orthorhombic and isomorphous Seignette salts the sodium-potassium tartrate has the optic axial plane parallel to the brachy-pinacoid, whilst in the sodium-ammonium salt it is parallel to the macro-pinacoid. Mixed crystals of the two salts show, as would be expected, the optic axes for different colours in two planes at right angles (as in brookite), but only after the crystals have been prepared for some time. Freshly-prepared mixed crystals exhibit crossed dispersion of the monoclinic type (as in borax). A maximum angle of  $75^\circ$  between the axial planes for red and violet light is given by crystals containing 45 per cent. Na-K tartrate. On standing, the axial planes slowly migrate to the planes of symmetry, and equilibrium is established in from two to thirteen weeks, this being hastened by increasing the temperature.

COLONEL N. T. BELAIEW, *On the Genesis of Widmanstätten Structure in Meteorites and in Terrestrial Alloys.*

The Widmanstätten structure belongs to the triad of secondary structures, the other two being the structure of large crystals and the network structure. Under suitable conditions either of these structures may occur in iron-carbon alloys, or in any other alloys crystallising in the face-centred cubic lattice and exhibiting the same kind of equilibrium diagram. As the diagram of the Fe-Ni alloys is quite similar to that of Fe-C, the same kind of crystallisation may be expected in either case and also in that of meteorites. The well-known Widmanstätten figures in meteorites are also arranged in a Widmanstätten structure. From their appearance an inference can be made as to the conditions of cooling which furthered their appearance. These conditions are a very slow cooling after solidification in the granulation zone and a relatively rapid

separation of the constituents afterwards in the zone of secondary crystallisation leading to their lodging themselves parallel to the octahedral planes in every granula.

PROF. L. R. WILBERFORCE, *Illustration and detection of inclined and horizontal dispersion in Bi-Axial Crystals.*

If the optic picture of an ordinary bi-axial crystal is viewed through a prism whose refracting edge is parallel or perpendicular to the axial plane, the appearances characteristic of horizontal and inclined dispersion are respectively produced. Such dispersions in a crystal, if too small to be detected by direct observation, can be discovered by thus using a prism of small angle alternately to reinforce and oppose them, and noting the want of symmetry in the effects produced.

ARTHUR RUSSELL, *On the occurrence of the Rare Mineral Nadorite in Cornwall, and of Beraunite (Eleonorite) in Co. Cork, Ireland.*

A single specimen of the rare mineral nadorite was found by the writer at the small antimony mine Bodannon, St. Endellion, Cornwall. The nadorite forms aggregates of nearly square platy crystals, transparent, of a yellowish-brown to reddish-brown colour, occupying a cavity in fibrous jamesonite. The crystals are combinations of a (100) and r (130), and are twinned on l (011). A very well-defined specimen of the variety of beraunite known as eleonorite was found by the writer at the iron and manganese mine of Roury Glen, Glandore, Co. Cork. It consists of a mass of diverging fibrous crystals of a reddish-brown colour, between walls of limonite. The fibres are elongated in the direction of the b axis, and show very strong pleochroism.

A. F. HALLIMOND and F. R. ENNOS, *On Stilpnomelane from North Wales.*

A dark scaly vein-mineral, strongly resembling biotite, proves on analysis to contain very little potash, and is very similar in physical properties to stilpnomelane from Moravia. The composition agrees with the formula:  $6\text{SiO}_2 \cdot 2\text{Fe}_2\text{O}_3 \cdot 2\text{FeO} \cdot 3\text{H}_2\text{O}$ . Sp. G. 2.85. Apparently uniaxial;  $\omega = 1.687$ ,  $\epsilon = 1.595$ . Pleochroic,  $\omega =$  dark brown,  $\epsilon =$  pale yellow. Brittle, with eminent basal cleavage and marked cleavage normal to this, yielding pleochroic chips.  $H = 3.5$ . Insoluble in hot N/2 HCl.

DR. G. T. PRIOR, *On the Chemical Composition of the Ashdon Meteorite.*

This meteoric stone, which fell at Ashdon, near Saffron Walden, Essex, on March 9, 1923, is a white hypersthene-chondrite containing  $8\frac{1}{2}$  per cent. of nickeliferous iron in which the ratio of iron to nickel is about 6.

### CORRESPONDENCE.

#### THE COLOURING OF POISONS.

To the Editors of THE CHEMICAL NEWS.

SIRS,—In a recent communication, under the above heading, Mr. James Sexton, M.P., advocates the colouring of poisons, and mentions several points against it put forward by the General Medical Council. He winds up with the words, "These four objections may be just or they may not. What I submit is that they are matters of policy to be determined by Parliament in open debate rather than settled autocratically by the most conservative of our trade unions."

Mr. Sexton has left out the most important people concerned in this matter. I refer to — I was going to have said "the chemists"—but to a Member of Parliament or one of the legal profession this word would, according to law, designate a pharmacist, who keeps open shop: it would, of course, include him, but I mean it in the wider sense of the "chemical profession." If Mr. Sexton does not know what I mean I shall be happy to explain it privately to him, if he so wishes.

I say he has left out the chemical profession; those men, or the followers of those men, who have discovered or synthesised the greater number of the poisons. Our contention is that if one poison is to be coloured, others will follow, and where is it to end? Mr. Sexton uses the expression "deadly poison"; what does he mean by that? He mentions one alkaloid, viz., strychnine; is this class of substance the one he calls "deadly poison," or would he also include prussic acid and the cyanides, compounds of arsenic including organic ones, mercurous and mercuric chlorides, lead acetate, phosphorus, etc.? Many of these are quite as poisonous as strychnine. If these are included, then try and imagine carrying on in a chemical laboratory with the KCN solution coloured with, say, gentian violet, and the HgCl<sub>2</sub> solution with malachite green. The alkaloids are detected

chiefly by means of colour reactions, with which a colouring matter might seriously interfere, especially where students are concerned.

Parliament is notoriously unscientific, otherwise it would not have permitted for one day the importation of cotton into Germany during the war; therefore with all due respect to it, Parliament is not able to give a properly considered decision upon this matter, without first taking council with the chemical profession.

In the event of this matter becoming the law of the land, Mr. Sexton will be doing his bit towards the advancement of science, if he will do his best to have a clause inserted in the Act, permitting all chemical and other scientific laboratories, whether public or private, and those firms which supply them, to obtain, easily and without red tape, any uncoloured chemical, whether poisonous or not. We are put to no end of trouble, as things are, to obtain a little duty free absolute alcohol for use in unpaid research work, the expense of the latter falling upon the person doing the research, but which the Inland Revenue calls "a hobby" and refuses to allow the deduction of the income tax on such expense.

I mention these things to show how we are hampered in ways that were not intended by Parliament, and we wish to avoid, if possible, this further and probably more serious difficulty.—Yours, &c.,

HERBERT HENSTOCK, M.Sc., Ph.D.,  
F.I.C.

*Chemical Research Laboratory,  
School Gardens,  
Shrewsbury.*

### NOTICES OF BOOKS.

*The Expert Witness*, by C. A. MITCHELL, M.A., F.I.C. Pp. XV. + 188. Cambridge: Messrs. Heffer & Sons, Ltd. 1923. 7s. 6d. net.

Chemists are very apt to engross themselves in their subject, and to leave to mere chance the important task of bringing to it and them a proper recognition of the high order of their work.

It is therefore only in times of great stress that such recognition is forthcoming, and by their own attitude chemists have themselves to thank for this.

In his latest work on the applications of science (and of art) to human identifica-

tion, criminal and other investigations, and to history, Mr. Mitchell has done his fellow workers a good service. This book is intended as much for the general public as for the scientific reader. It is eminently entertaining and interesting, and the reviewer's regret was on reaching the last page.

Expert evidence in general is discussed, and then the author deals with such specialised cases as the identification by skin-prints, medical, scientific and bacteriological evidence. The role of the expert in handwriting and in art, and the applications of such specialised evidence, is very ably described, with the aid of many illustrations.

The application of chemical knowledge in the investigation of documents and writings has hitherto not received adequate attention. The author directs attention to a number of recent investigations in legal cases where such chemical evidence was invaluable.

Doubtless these will become more and more numerous when it is more widely realised what a valuable part chemistry can play in such matters. J.G.F.D.

*Landscape and History*, 1s. London: Simpkin, Marshall, Hamilton, Kent & Co., Ltd.

The anonymous author has addressed this little volume more especially to the readers (and distinguished writers) of the various *Outlines* now appearing.

He makes apposite quotations from Mr. H. G. Wells' address before the British Science Guild last year, and his theme is apparently to draw attention to the geological and historical importance of veins and strata of iron. These, it is urged, possess very great significance to an extent by no means fully realised in scientific circles. Six excellent photographs are included.

The Institute of Science and Industry of Australia has issued Bulletin No. 24, entitled *The Production of Liquid Fuels from Oil Shale and Coal in Australia*, by R. E. THWAITES, M.A.

It is pointed out that the rapid depletion of the world stocks of petroleum and the extraordinary increase in the use of oil-fuels, and the advancing efficiency of oil-engines have awakened a recognition of the importance of all questions touching the economic production of liquid fuels. The necessity of the direct value of researches into their production is universally recognised. In

Australia the question whether natural petroleum exists in payable quantities or not is unsettled, but large supplies of coals and shales certainly exist.

Apart from their direct economic value, they have also that which arises from the possibility of making the country independent of foreign supplies.

The present Bulletin embodies the results of the inquiries made. For some years past Mr. Thwaites has made a special study of fuel problems, and has also carried out experimental investigations on the distillation of coal and the production of liquid fuels therefrom, both in small and large scale plant.

The Ministry of Agriculture and Fisheries has issued a leaflet, No. 316, dealing with the cultivation of lavender for marketing and distilling. Lavender has been grown commercially in the south of England for a great many years, having been introduced in 1568, and where the soil and situation are favourable, there is no doubt that it is a profitable crop and worthy of consideration. It is grown for the oil for perfumery, for sale in a fresh state as "bunched lavender," and as "dried lavender" for sachet making, etc. As regards oil production, it is pointed out that chemistry has not yet succeeded in producing a synthetic product which can claim to be a substitute for English oil of lavender, and hence the supply depends wholly upon the natural product.

#### BOOKS RECEIVED.

*The Chemical Elements*, by F. H. LORING. Pp. VIII. + 171. 1923. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C. 8s. 6d. net.

*Konduktometrische Titrationen*, von DR. I. M. KOLTHOFF. Pp. VI. + 94. 1923. Verlag von Theodor Steinkopff, Residenzstr. 12b, Dresden, Blasewitz. 2s. 9d.

*The Development of the Sciences*, by ERNEST WITHAM BROWN, HENRY ANDREWS BUMSTEAD, JOHN JOHNSTON, FRANK SCHLESINGER, HERBERT ERNEST GREGORY, LORANDE LOSE WOODRUFF. Pp. XIV. + 327. 1923. Humphrey Milford, Oxford University Press, Amen Corner, E.C.4. 16s. net.

*A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, by J. W. MEL-

LOR, D.Sc. Pp. X. + 1074. Vol. IV., 1923. Messrs. Longmans, Green & Co., 39; Paternoster Row, E.C.4. 63s. net.

*Elektrochemie Nichtwässriger Lösungen*, von PAUL WALDEN. Pp. XI. + 515. 1924. Herr Johann Ambrosius Barth, Dorrienstrasse 16, Leipzig, Germany. Bound 28s., unbound 24s.

*Organische Chemie*, von DR. RUDOLF PUMMERER. Pp. XI. + 209. 1923. Verlag von Theodor Steinkopff, Residenzstr., 12b, Dresden und Leipzig. 4s.



This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

*Latest Patent Applications.*

- 27376—Albert, A.—Process for producing organic compounds of mercury. Oct. 31.  
 27233—Cassella & Co., Ges. L.—Production of acridinium compounds. Oct. 30.  
 27048—Chance & Hunt, Ltd.—Treating crude oxide and carbonate of zinc. Oct. 29.  
 27219—Farbwerke vorm. Meister, Lucius & Bruning.—Manufacture of acid azo-dyestuffs. Oct. 30.

*Specifications Published this Week.*

- 205141—Robinson, C. S.—Recovery and refining of sulphur.  
 205288—Goodwin, C. J.—Manufacture of oxides of nitrogen and nitric acid.  
 205301—Weymann, G.—Drying of ammonium sulphate.  
 197315—Compagnie de Bethune Soc. Anon.—Manufacture of ethyl alcohol from sulphovinic acid.  
 205528—Machay, H. S.—Method of and means for roasting metallic ores.  
 205563—Chemische Fabrik Greisheim Elektron.—Process for the production of aluminium chloride and alumina.  
 191363—Pereira, H.—Process for manufacturing dioxyperylene.  
 194719—Consortium für Elektrochemische Industrie Ges.—Manufacture of anhydrides of fatty acids of low molecular weight.

*Abstract Published this Week.*

- 203749—Sodium silicate.—Clayton, W., of Arderry, Allerton Drive, Mossley Hill, Liverpool, and Richards, H. W., of 9, Hawarden Avenue, Wallasey, Cheshire.

Sodium silicate solution is evaporated by spraying into heated air. The solution may be of 100° Tw. and may contain 2.1 parts by weight of silica to 1 part by weight of Na<sub>2</sub>O. The spraying may be effected with the liquid at 45° C. by means of an air pressure of 65 lb. per sq. in. Beneath the jet of liquid is a high velocity air jet at right angles to the liquid jet as in milk spraying, a pressure of 150 lb. per sq. in. being suitable. Instead of an air jet superheated steam or fine gases may be used.

Messrs. Rayner Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

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# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3320.

## ARE THE NATURAL GROUPINGS OF THE ELEMENTS AND THE SPECTRAL LINES OF HYDROGEN RELATED?

### PART IV.

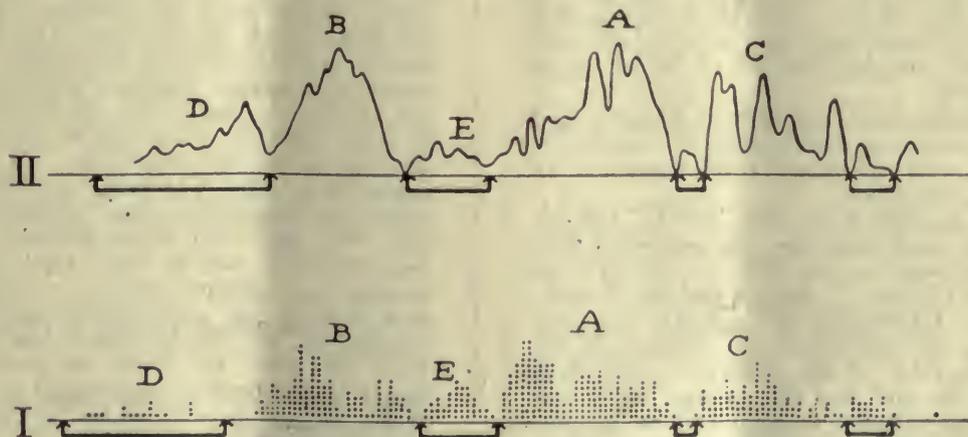
By F. H. LORING.

In continuing the study—see *The Chemical News*, 1923, CXXVII., pp. 225, 257, 272, 290—attention should again be drawn to the planetary bodies, in particular the minor planets, or asteroids as they are commonly called (see Part III.); as there is some likelihood of the distribution of these small bodies in space following a place law similar to the distribution of lines in the hydrogen spectrum. With this view in mind the writer has examined the distribution of the minor planets as given in the *Encyclopædia Britannica*, 1911, 11th Edition, Vol. XXI., p. 717.

In the accompanying diagram, I. shows the distribution as given in the *Encyclopædia*, while II. (explained below) is taken from Sommerfeld's "Atomic Structure and Spectral Lines," p. 210. The letters and brackets are added by the present writer for purposes of comparison. It will be seen how closely the maxima and minima coincide in these two curves, like letters indicating similar characteristics, and the brackets indicate minimum values and gaps. In the diagram (II.) representing the hydrogen spectrum, the place where the  $\alpha$  line would

fall is on the left side, and similarly the planets occur in greater orbits as one proceeds from right to left, the base line, if continued, passing through the sun. In both cases the highest points occur at A.

In explanation of the curve (II.) for hydrogen, the following from Sommerfeld's book, pp. 209, 210, will make the matter clearer: "Besides the Balmer spectrum to be understood in the general sense of equation (5), hydrogen possesses another spectrum of quite a different nature, the so-called 'many-lines spectrum' (*Viellinienspektrum*). In contradiction to Balmer's 'four-line' spectrum (called so, occasionally in view of its four lines  $H_{\alpha}$ ,  $H_{\beta}$ ,  $H_{\gamma}$ ,  $H_{\delta}$  in the visible [though some writers include the He line which is in the ultra-violet]), the many-lines spectrum is to be regarded as a *band spectrum*, although it does not exhibit the external signs of band-spectra, namely, the accumulation of the lines at certain heads of the bands and the repetition of these bands, constituting flutings. From the great number of lines observed, however, individual groups of lines may be separated out, which follow the laws of band lines (set up by Deslandres—see Fulcher, *Physikal. Zeitschr.*, 1912, p. 1140; Crose, *Ann. d. Phys.*, I., p. 37), and which also show themselves to be related in that they behave similarly in the Zeeman effect. The many-lines spectrum arises in the Geissler tube at lower discharging potentials than the Balmer spectrum. The question as to the carrier of the many-lines spectrum is a subject of great controversy. The later experimental investigations, in particular a work of E. Gehreke (Cf. *Report of the Physikal.-Techn. Reichsanstalt*, 1921) leave no



room for doubt that its carrier is the hydrogen molecule and not the hydrogen atom. From the point of view of theory, only the  $H_2$  molecule can come into question at all as the carrier of the many-lines spectrum, on account of the great complexity of the latter. Actually, we shall see in Chapter VII. that the modern theory of band-spectra, even if it cannot predict quantitatively the frequencies of the many-lines spectrum, it can at least completely account for its general character qualitatively if its calculations are based on the mass and size of the  $H_2$  molecule. To give the reader at this early stage a general survey of the distribution and density of the lines, we give here as a résumé of the empirical data the accompanying curve [II.] that has been calculated and drawn by K. Glitscher (*Sitzungsber. d. bayer. Akad.*, 1916, p. 125). At regular intervals of 100 wave-numbers it gives as ordinates the total intensity of the lines that have been measured in each of these intervals, and the intensity of which has been estimated. The end-points of the ordinates have been connected by a smooth curve. This curve is the schematic picture of the distribution of intensity in the many-lines spectrum, and would be obtained directly if, for example, the action of the Balmer lines were eliminated and the whole spectral region were photographed with a greater width of slit and measured photo-metrically."

Commenting on the above, it will be seen that the development of this study is in general harmony with the foregoing deductions; and the inference is that the law of distribution, whether it involves electrons, atoms, molecules, minor planets, or planets, is of common origin; and, as was already stated in Part II., the law of the part is the law of the whole. Strictly speaking, perhaps one should say that the law of the part is translatable into the law of the whole, or *vice versa*.

This idea may seem strange to many who have not followed the trend of modern research in directions that point in some ways to this conclusion.

Now to show here this "trend," the following, taken from the *Encyclopædia Britannica*, supplement, 1922, vol. XXXII., p. 561, will suffice: "*Spectra and the Periodic Table*.—Attention is being drawn more and more to the relation of the spectrum to the periodic table of the elements. While it cannot be said that the relation is known with any approach to completeness, a number of important facts have been noted

which may ultimately prove of great service in the interpretation of the table. It has long been known that, when doublets or triplets occur in the spectra, the wave-number separations of their components (which are constant in the sharp and diffuse series) are approximately proportional to the squares of the atomic weights of the elements producing the spectra—so long as those elements belong to the same family group. The Zeeman effect also is generally the same for lines of corresponding series in the spectra of elements belonging to the same group. But perhaps the most comprehensive connection of spectra with the periodic table is established by the 'displacement law' of Kossel and Sommerfeld (*Verh. Deut. Phys. Gesell.*, 1919). It has been observed that the 'complexity' of the lines of a series—*i.e.*, their character as singlets, doublets, or triplets—is constant throughout a group, but varies from one group to another. The displacement law states that, when an element is ionised, the enhanced series takes on the same type of complexity as the arc series produced by the element to the left (*i.e.*, in the preceding group) in the periodic table. It is assumed that electrons arrange themselves round the nucleus in rings, and that spectrum phenomena are produced by electrons in the outer ring. If the outer ring contains an odd number of electrons, the spectrum will show triplets and singlets. In the periodic table each element contains one outer electron more than its neighbour in the preceding group, while a group consists of elements having the same number of electrons in the outer ring. It follows that the removal of an electron from an element [atom] will make the outer ring similar to that of the immediate forerunner of the element in the table, and so make the enhanced lines of the first element of the same type of complexity as the arc lines of the second. Removal of a second electron would restore the arc type of complexity, for the number of outer electrons would again become odd or even, as the case might be. A second ionisation is difficult to bring about in most cases, but with silicon it is probable that one, two, and even three electrons have been removed, step by step, thus making possible four distinct spectra. These appear to show the alteration of complexity required by the displacement law. The table here gives the types of series produced by the neutral and ionised elements of the various groups, so far as they are known at present."

Group	.....VIII. or O.	I.	II.	III.	IV.	V.	VI.	VII.
Arc	.....N.C.A.	D.	T. & S.	D.	T?	D?	T.	(?)
Enhanced	.....(?)	N.C.A.	D.	T. & S.	D?	T?	D?	T?

N.C.A. = not completely analysed. S = singlets. D = doublets. T = triplets.

"The spectra of the higher groups are much more complex than those of the lower ones. Their series, if they possess any, are possibly of a different type from those with which we are familiar. The displacement law, however, suggests that by repeated ionisations, series—and therefore terms—might be detected in each spectra, of the same kind as those of the groups of elements on the left. But since, with each successive ionisation, the term constant, N, is multiplied in the ratio 1:4:9:16, etc., the chief series lines might tend rapidly to approach the far ultra-violet and become difficult to observe."

#### SUMMARY OF PARTS III. AND IV.

It was shown that the radial distribution of the planets, taken in mean distances from the sun in millions of miles divided by 10, corresponded for a consecutive series of

planets with the  $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $\epsilon$  group numbers of the periodic table, which can be derived from the five correspondingly lettered lines of the Balmer spectrum of hydrogen.

It is here shown that the distribution of the minor planets in groups follow somewhat closely the line-intensity curve of the many-lines spectrum attributed to  $H_2$  as the carrier; and these studies seem to show that the law of the part can be transformed into the law of the whole or *vice versa*, so that the law of distribution, whether it involves electrons, atoms, molecules, minor planets, or planets, is of common origin; and underlying all this phenomena there seems to be something that may be referred to as a "place principle." It is of course known that all the minor planets have not been discovered, their number being of the order of 1,000, but a sufficient number are known to show a characteristic type of distribution as indicated by the diagram.

## INDIGOID DYESTUFFS.

### PART I.

By R. F. HUNTER, F.C.S.

Some months ago (see *The Chemical News*, July 13, this Vol. pp. 17-18), an article was published on "Sulphur Dyes." It is now proposed to deal in something of the same way with some of the other important classes of synthetic colouring matters, and the first group to be dealt with is the indigoid dye family. It is not intended to deal exhaustively with the subject, but only a few standard compounds will be dealt with. The practical side of the preparations will not be considered, since it has been very fully dealt with in the last two chapters of Thorpe and Ingold's "Vat Colours."

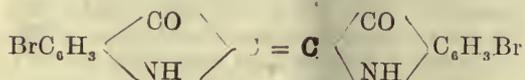
Before proceeding to the subject proper, it might be of interest to give the historical side of indigoid dyestuffs some consideration.

The famous Tyrian purple, or rather "the purple of the ancients," is the only

vat dye which we have records of for some fifteen hundred years before the Christian era. The colour was obtained from an excretion from certain shell fish found along the coasts of Tyre. This dye was the most prized of colours, and regarded as an emblem of royalty, and fit for the highest services of religion. By combining the infusions of different kinds of shell fish, the Phœnicians were able to vary the colour, some shades tending toward red and some toward blue, the two shades most mentioned in the English versions of the Old Testament being described as "blue" and "purple." Accounts of the manufacture of this substance are given by various Latin writers, among whom we might mention Cassidorus, Pollux, Vergil, Lucretius, and Pliny. Probably the colour was introduced into Europe about 500 B.C. The Greeks paid considerable attention to colours, the Romans obviously obtaining their knowledge of colouring matters from the Greeks. During the Middle Ages, the knowledge of purple was lost, save in the writings on the ancients. Canniparius, writing in Italy at

the beginning of the 17th century, speaks of the purple as being known only through ancient writings.

Cole made observations on the subject in the *Phil. Trans.* 1685. Réaumur in 1710 (in *Mem. de l'Acad. Royale des Sciences*, 1711) made an observation on a number of purple-giving molluscs on the coast of Poitou. Duhamel, in 1736, recorded similar observations in the same scientific paper. Bancroft made some investigations on the subject in 1813. Schunk (1879) investigated the substance. Friedlander took up the subject in 1907. He isolated the colouring matter, preparing 1.4 gm. of pure substance from the glands of 12,000 specimens of the *Murex brandaris*. The substance was insoluble in alcohol, ether, ligroin, chloroform, acetic acid and acetone; soluble with difficulty in hot pyridine, in which it dissolved to give red violet solutions. Analysis indicated the formula  $C_{16}H_8Br_2N_2O_2$ . This represents 2:8-dibromoindirubins and 1:6-dibromoindigos. The substance was found to be identical with 6:6' dibromoindigo previously synthesised by Sach's and Kemp from p bromo o nitro benzaldehyde:



6:6' Dibromoindigo.

We now come to the question of natural indigo. From the earliest times the indigo plant was cultivated and the indigo extracted from it by the Hindus. Its preparation is described in old Sanskrit scripts, and these scripts show that its mode of preparation scarcely underwent any alteration during the centuries preceding the discovery of India by the Dutch.

From India the knowledge of indigo spread along the trade routes through Persia to Syria and Arabia and thence to Egypt. The Egyptians used indigo extensively. This is revealed by analysis of mummy cloths. The knowledge of indigo reached China about 700 A.D. From Egypt the knowledge passed to Greece, and thence to Rome. During the dark ages between 500 to 1200 A.D., the knowledge was almost lost in Europe save in a few Italian cities. From Italy the knowledge spread to France and Flanders during the thirteenth century. The Flemish and Italian dyers using indigo in the fourteenth century unfortunately excited the enmity of the older society of Black Dyers. The feud con-

tinued well into the sixteenth century, and the Black Dyers were so successful that indigo was prohibited as being a newly invented, deceitful, eating and corrosive dye. The Dutch, after 1602, however, began to import large quantities of indigo, and the superiority of this caused it to take the place of the woad industry to an enormous extent. In France the use of indigo was allowed when mixed with a hundred times its weight of woad in the "woad vat."

The principal plants cultivated for the purpose of obtaining indigo belong to the genus *Indigofera*, and have been grown in India, China, Japan, Java and the Philippine Islands, Central America and the West Indies, Brazil and Madagascar.

The principal species are:—

*Sumatrana*,  
*Acreta*,  
*Paucifolia*,  
*Tinchloride*,  
*Secundiflora*,  
*Disperma*, and  
*Argentea*.

The colour-forming principle in the *indigofera* is a glucoside of indoxyl, indican, which, by the action of enzymes present in the plant, is hydrolysed, yielding free indoxyl. This, by atmospheric oxidation, proceeds to indigo. The manufacture of indigo (natural) hence consists of the two essential operations: firstly, the steeping of the plant in water when fermentation takes place and hydrolysis of the glucoside follows; secondly, the precipitation of the colouring matters from the solution of indoxyl by the action of air. The chemicals used in the manufacture of natural indigo have three purposes: first, to purify the water for steeping; secondly, as an adjunct for steeping; and lastly, in the oxidising process.

Natural indigo contains, as well as indigo and indirubin, traces of uncondensed isatin, a yellow colour which has been isolated and identified as the tetrahydroxy flavone; k mpborol and a number of brown amorphous bodies which dissolve in alkaline reducing solutions but cannot be used to colour cotton fibre. There is also present a horn-like substance known as indigo gluten, and certain mineral matter. The most important constituent of the natural substance from the point of view as a dye is indigo or indigotin, the dyeing properties of which are due to its capability of passing into a leuco compound, "indigo white," in

solution when treated with alkaline reducing agents. In alkaline solution this penetrates the fibres of cotton, and is reoxidised to indigo by atmospheric oxidation dyeing the fibre. Indirubin undergoes similar conversion with alkaline reducing agents.

We now come to consider one of the most important questions of to-day, *viz.*, synthetic indigo. In 1841, Erdmann and Laurent oxidised indigo to isatin. Laurent, by chlorination and bromination of this, isolated mono and dichloroisatin and dibromoisatin. Bayer commenced his researches on isatin in 1865 in conjunction with Knop, attempting to reduce the substance to indigo. The attempt failed, but resulted in the isolation of dioxindole and oxindole. He regarded oxindole as a phenol of a substance,  $C_6H_4 : C_2H_3N$ , to which he gave the name indole, and reduced oxindole to indole in 1866 by passing the vapour of oxindole over heated zinc dust.

In 1878 Bayer synthesised isatin by the scheme suggested originally by Kekulé. Starting with phenylacetic acid, he converted this into successively nitrophenylacetic acid, aminophenyl acetic acid, oxindole, nitro oso oxindole, amino oxindole, and finally this, with ferric chloride, into isatin.

Indigo had been obtained in traces by Emmerling by distilling o nitro aceto phenone with zinc dust and soda lime. This reaction was shown by Bamberger to depend on the intermediate reduction product methylanthranol. The first rational synthesis of indigo was accomplished when Bayer synthesised isatin, for Bayer and Emmerling had shown in 1870 that isatin can be reduced to indigo by treatment with  $PCl_5$ , followed by contact with atmosphere. This, however, was improved a year after the isatin synthesis by Bayer, who prepared isatin chloride by the action of phosphorus pentachloride on isatin, and reduced this by means of hydriodic acid to indigo in acetic acid solution.

A year later, Bayer obtained indigo from o nitro cinnamic acid by the following scheme: By the action of KOH on the dibromide he obtained o nitro phenyl propionic acid. This, on heating with alkalis, is converted into isatin, and by heating with alkalis in the presence of glucose is converted into indigo. Also, the ethyl ester of o nitro phenyl propionic acid, on treatment with  $CO_2H_2SO_4$ , proceeds to the isomeric ester of isatogenic acid. This, on hydrolysis, passes into the acid and then into isatin,

and on reduction yields the ethyl ester of indoxyl acid. The free acid, on heating, loses  $CO_2$  and passes into indoxyl, and this, on oxidation, passes into indigo.

(To be continued.)

## PROCEEDINGS AND NOTICES OF SOCIETIES.

### THE ROYAL SOCIETY.

THURSDAY, NOVEMBER 22.

SPECIAL GENERAL MEETING TO CONSIDER THE ANNUAL REPORT OF COUNCIL.

Papers read:—

F. SIMEON, *The Carbon Arc Spectrum in the Extreme Ultra-violet.*—II. Communicated by Prof. A. W. Porter, F.R.S.

The results may be summarised as follows:—

(1) The spectrum of the carbon arc in vacuum extends as far in the extreme ultra-violet as that of the spark, with the exception of a very faint line at 360.5 Å, and about 25 lines have been added to the arc spectrum as already recorded.

(2) The L series of carbon can be excited by a potential of between 30 and 40 volts.

(3) Reasons are given for thinking that a number of lines in the carbon spectrum are true "arc" lines.

(4) Providing the grating will give radiation in the short-wave region, the same technique suffices to photograph the spectrum from 1850 Å to 370 Å.

H. J. GOUGH and D. HANSON, D.Sc., *The Behaviour of Metals subjected to Repeated Stresses.* Communicated by Sir Joseph Petavel, F.R.S.

The subject of the paper is the effect of static and alternating stresses on the micro-structure of metals, the main object of the research being to determine whether the crystalline structure of a metal can be affected when subjected to ranges of stress less than the limiting range of stress (fatigue range). It is shown that with "Armeo" iron, mild steel, and copper, crystalline "slip" occurs at ranges of stress considerably less than the fatigue range.

In explanation of this result, it is suggested that metals can be "strain-hardened" under the action of alternating stresses, as

well as under static stresses; it is further suggested that fracture occurs, in a metal subjected to alternating stresses, when a certain limiting strain for the material is exceeded.

The paper is divided into the following sections:—

- (1) Preliminary Mechanical Tests.
- (2) Study of the Microstructure under Static Stresses.
- (3) Study of the Microstructure under Alternating Stresses.
- (4) Discussion of the Results with respect to other known Phenomena of the Fatigue of Metals.

W. SUCKSMITH and L. F. BATES, *On a Null Method of Measuring the Gyro-Magnetic Ratio*. Communicated by Prof. A. P. Chattock, F.R.S.

A new method is described of determining the gyro-magnetic ratio, and results obtained with it are given. As in the ordinary resonance method, the specimen, suspended vertically by a fine wire along the axis of a helix, is magnetised by an alternating current of same frequency as natural frequency of the system; but the resulting resonance amplitude is reduced to zero by a series of impulses timed to oppose those due to gyro-magnetic effect.

As no measurement of magnetic moment, frequency, or damping is involved, a considerable gain in precision is obtained. The method is independent of time-lag in magnetisation, and so can be applied to Heusler alloys.

The following table contains mean values of ratio obtained for iron, nickel and Heusler alloys:—

Metal.	K.
Iron .....	0.503
Nickel .....	0.501
Heusler alloys .....	0.501

The number is in every case 0.5 within the limits of experimental error, and corroboration is thus afforded of measurements of the ratio recently carried out in this University by an independent method by Messrs. Chattock and Bates.

J. H. SHAXBY, *Studies in Brownian Movement.—II. The Determination of Avogadro's Number from Observations on Bacteria (Cocci)*. Communicated by Prof. S. W. J. Smith, F.R.S.

A determination of Avogadro's number by the method of measuring the displacements, due to their Brownian movements,

of small spheres suspended in water, was carried out with cocci. Their surfaces may fairly be supposed to be "wettted" so that there is no slip between the water immediately adjacent and the spheres themselves, and the resistance which might arise from electrical sources depending on slip is avoided. Precautions were taken that no movements other than Brownian should be recorded. The value of N thus found, from the large number of observations made on *Staphylococcus albus*, is  $6.08 \times 10^{23}$ .

Papers read in title only:—

H. HARTRIDGE, Sc.D., and F. J. W. ROUGHTON, *The Kinetics of Hemoglobin.—II*. Communicated by Prof. J. N. Langley, F.R.S.

A. F. A. YOUNG, *The Thermionic and Photo-Electric Properties of the Electro-Positive Metals*. Communicated by Prof. O. W. Richardson, F.R.S.

O. F. T. ROBERTS, *The Theoretical Scattering of Smoke in a Turbulent Atmosphere*. Communicated by Dr. G. C. Simpson, F.R.S.

#### THE ROYAL SOCIETY OF ARTS.

On Monday, November 19, the Cantor Lecture (II.), entitled *The Cultivation of Cocoa in British Tropical Colonies*, was given by SAMUEL HENRY DAVIES, M.Sc., F.I.C.

On Wednesday, November 21, at the Ordinary Meeting, a paper entitled *Forgeries of Ancient Stained Glass* was read by J. A. KNOWLES. The Right Hon. the Earl of Crawford and Balcarres, K.T., P.C., F.S.A., presided.

On Tuesday, November 27, at the meeting of the Dominions and Colonies Section, a paper entitled *The West Indies* was read by the VISCOUNT BURNHAM, C.H., LL.D., D.LITT., M.A. The Lord Askwith, K.C.B., K.C., D.C.L., Chairman of the Council, presided.

On Wednesday, November 28, at the Ordinary Meeting, a paper entitled *The Effect of Sun, Sea and Open Air in the Treatment of Disease* was delivered by SIR HENRY JOHN GAUVAIN, M.A., M.D., M.Ch., Medical

Superintendent of the Lord Mayor Treloar Cripples' Hospital. Lord Dawson of Penn, G.C.V.O., K.C.M.G., C.B., M.D., F.R.C.P., M.R.C.S., presided.

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SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

The next meeting of the Society will be held on Wednesday, December 5, at the Chemical Society's Rooms, at 8 p.m.

The following papers will be read:—

*Crystalline Bromides of Linseed Oil*, by HAROLD TOMS, M.Sc. (under the Analytical Investigation Scheme).

*The Plea for Standardisation*, by M. S. SALAMON, B.Sc.

*Note on the Estimation of Chromium*, by HUBERT T. S. BRITTON, M.Sc., F.I.C.

*The Colorimetric Estimation of Lead in Cream of Tartar*, by R. L. ANDREW.

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PHYSICAL SOCIETY OF LONDON.

A meeting of the Society was held on Thursday, November 29.

A joint discussion with the Institution of Electrical Engineers took place on the subject of "Loud Speakers for Wireless and other Purposes."

FIRST SESSION OF DISCUSSION.

*General Principles involved by the Accurate Reproduction of Sound by Means of a Loud Speaker*, by PROF. A. O. RANKINE.

*Theory of Loud Speaker Design*. (Some factors affecting faithful and efficient reproduction. Causes of inefficiency. Economy in amplifiers resultant on improved efficiency. With demonstration). By DR. L. C. POCOCK.

*The Electrical Side of the Phenomena of Low-frequency Amplification in Wireless Circuits*. Causes of distortion and means of elimination. Demonstration. By PROF. C. L. FORTESCUE.

*The Problem of Distortion in the Reproduction of Sound by the Gramophone*, by MR. H. L. PORTER.

General Discussion.

SECOND SESSION OF DISCUSSION.

*Distortion in Audio-Circuits*. Relative importance of various frequencies. Demonstration of effect of elimination of various frequency bands. Demonstration of nodes and anti-nodes in an auditorium. *Methods, direct and indirect, of Measurement of the Efficiency and Faithfulness of Loud-Speaking Telephones*. By MR. E. K. SANDEMAN, B.Sc.

*The Overtones of the Diaphragm of a Telephone Receiver*. Their effect in causing distortion. With Demonstration. By PROF. J. T. MCGREGOR-MORRIS and PROF. E. MALLET.

*Architectural Acoustics*. Its relation to Loud Speaker operation. By MR. G. A. SUTHERLAND, M.A.

*Some Directions of Improvement of the Loud-Speaking Telephone*. Action of the Frenophone. With Demonstration. By MR. S. G. BROWN, F.R.S.

*The Characteristics of the Gaumont-Lumière Loud Speaker*. With Demonstration. By CAPT. P. P. ECKERSLEY.

General Discussion (continuation of).

Visits were arranged, by kind permission of the British Broadcasting Company, to their Studio on Savoy Hill.

Proceedings at the meeting on November 9, Alexander Russell, M.A., D.Sc., in the chair:—

A Demonstration of *Experiments on the Reproduction of Vowel Sounds* was given by SIR RICHARD PAGER.

The author found that each of the vowel sounds comprises two components lying within two ranges two or three semitones in extent, the two ranges being characteristic of the vowel and separated by an interval of from three tones to three octaves, according to the nature of the vowel. The devices shown for reproducing vowels consisted in their simplest form of pairs of resonators tuned to the tones characteristic of various vowels and so arranged that the sound from

an artificial larynx or squeaker could be passed through them in series or in parallel. Certain vowels in which the upper resonance is a harmonic of the lower can be produced by means of a single resonator. Consonants are found to depend in part on characteristic resonances and their rate of change, and in part on the release of air pressure in the compound resonators, some of which were caused to emit words by opening and closing their orifices suitably by hand. The author, in illustration, arranged his hands to form a double resonator in imitation of the human mouth, and passed through them the sound from a squeaker representing the larynx. By manipulating the fingers and hands, he was able to pronounce easily recognisable sentences.

A discussion followed.

A paper on *Scattering of Light by Carbon Dioxide, Nitrous Oxide, and some Organic Vapours*, by A. L. NARAYAN, M.A., A.INST.-P., was read by Lord Rayleigh in the absence of the author.

It has been shown by Lord Rayleigh that the light scattered laterally by the molecules of gases is not completely polarised, but contains a component polarised at right angles to the direction which is predicted by theory for a spherical molecule, the two components being conveniently referred to as the "wrong" and the "right" components respectively. The author was able to employ sunlight for illuminating gases and vapours, which he enclosed in a jointless tube. The strengths of the components were compared both by direct photometry, and by photometric comparison of their effects on a photographic plate, improved thermo-electric apparatus being employed for the latter purpose. Lord Rayleigh's results were confirmed, particularly in the case of  $\text{CO}_2$  and  $\text{N}_2\text{O}$ . It is suggested that the difference in the scattering power of these two gases is contrary to the prediction of the Lewis-Langmuir theory of the atom.

#### DISCUSSION.

Prof. A. O. Rankine said that his experiments, referred to, merely showed that the collision-area of the molecules in question varies with orientation in a manner consistent with the Lewis-Langmuir theory; it may be possible to invent other molecular models with which the experimental results will be equally consistent. These results, however, are relevant only to the external

form of the molecules, for viscosity may be presumed to be unaffected by the distribution of mass between the nuclei. Thus the masses of the nuclei would, according to theory, be 8, 6, and 8, in  $\text{CO}_2$ , and 7, 8, and 7, in  $\text{N}_2\text{O}$ ; and since, as Sir J. J. Thomson has suggested, these molecules would have different moments of inertia though their masses would be equal, it might be expected that they would differ in their polarising effect.

Mr. J. Guild said that in the measurement of such small intensities of light a large experimental error must be expected, so that the agreement between the author's and Lord Rayleigh's results was much better than might have been expected. Particularly in the case of vapours, where the percentage of the "wrong" component is small, the Nicol system is being used under the most disadvantageous conditions, which are calculated to evoke various defects even in the most perfect apparatus. As regards the photographic method of photometry, would not the actinic effects of the "right" and of the "wrong" components be different? In the case of the Tyndall effect due to larger aggregates, the intensities of the corresponding components are respectively proportional to the inverse fourth and the inverse eighth powers of the wave length, so that the "wrong" component would be much bluer than the "right" and have a disproportionate effect on the plate. The author mentions that many iridescent colours in Nature are due to scattering of light. It is interesting to note that many other common colours have been traced to the same cause, *e.g.*, the blues of the sky, of birds' feathers, and of the eyes of blondes.

Lord Rayleigh, in reply, said that he did not suppose the authors of the Lewis-Langmuir theory regarded their model as a real representation of the atom, consistent with all the latter's properties. It is rather a schematic diagram adapted to summarise certain groups of properties, and might well be inconsistent with others. The chromatic difference between the components in the Tyndall effect, though not completely accounted for, is a fact; but the effect is not comparable with that under discussion, the smallest particles which show the Tyndall effect being large compared with molecules. That there is no substantial chromatic effect on the photographic plates is proved by the agreement of the results of the



photographic method with those of direct photometry.

*On the Measurement of the Surface Tension of a Small Quantity of Liquid*, by ALLAN FERGUSON, M.A., D.Sc.

If a small quantity of liquid—one cubic millimetre or less—be placed in a vertical capillary tube, its surface tension may be determined by applying pressure to the upper end of the tube, and measuring the pressure necessary to force the liquid into such a position that the meniscus at the lower end of the tube is *plane*.

Interfacial tensions may also be determined in this way.

If no restriction be placed on the amount of liquid available, a simple apparatus may be used, by means of which the ordinary surface tension of a liquid, or the interfacial tension between two liquids, may be measured in several different ways.

#### THE GEOLOGICAL SOCIETY OF LONDON.

At the meeting on November 7, Prof. A. C. Seward, Se.D., F.R.S., President, in the chair, the following communications were read:—

*On the Skeleton of IGUANODON ATHERFIELDENSIS sp. nov., from the Wealden Shales of Atherfield (Isle of Wight)*, by the late REGINALD WALTER HOOLEY, F.G.S. Read by Dr. A. Smith Woodward, F.R.S., F.G.S.

*The Igneous Rocks of the Tortworth Inlier*, by PROF. SIDNEY HUGH REYNOLDS, M.A., Sc.D., F.G.S.

At the meeting held on Wednesday, Nov. 21, the following communication was read:

*The Development of the Severn Valley in the Neighbourhood of Iron-Bridge and Bridgnorth*, by L. J. WILLS, M.A., Ph.D., F.G.S. With a Section on the Upper Worfe Valley, in collaboration with E. E. L. Dixon, B.Sc., F.G.S.

#### THE INSTITUTION OF MINING ENGINEERS.

The thirty-fourth annual general meeting of the Institution of Mining Engineers was held on Thursday, November 29.

The following papers were read, or taken as read, and submitted for discussion:—

*Hydraulic Stowage at the Dalzell and Broomside Collieries*, by PROF. R. W. DRON, M.Inst.C.E.

*Some Effects of High Air-Temperatures upon the Miner*, by PROF. K. NEVILLE MOSS, M.Sc. (Sixth Report to the Committee on "The Control of Atmospheric Conditions in Hot and Deep Mines.")

*Strata Temperatures in South Wales, including Pembrokeshire*, by T. D. JONES, M.Sc. (Seventh Report to the Committee on "The Control of Atmospheric Conditions in Hot and Deep Mines.")

*The Specific Heat of Coal*, by G. COLES, B.Sc. (Eighth Report to the Committee on "The Control of Atmospheric Conditions in Hot and Deep Mines.")

The following paper will be submitted for further discussion:—

*The position of Mechanical Engineering in Colliery Operations*, by SIR WILLIAM ELLIS, G.B.E., D.ENG. (see *Trans. Inst. M.E.*, 1923-1924, vol. LXXVI., page 85).

#### THE OPTICAL SOCIETY.

##### THE 1923 THOMAS YOUNG ORATION.

A meeting of the Society was held at the Imperial College of Science and Technology, on Tuesday, November 27, when the Thomas Young Oration was delivered by Dr. M. von Rohr, Jena, the subject being *Contributions to the History of the Spectacle Trade from the earliest times to Thomas Young's Appearance*.

#### THE INSTITUTION OF ELECTRICAL ENGINEERS.

*Periodic Trigger Reception*, by E. V. APPLETON, M.A., D.Sc., and F. S. THOMPSON, B.A., Royal Corps of Signals.

The phenomenon of oscillation hysteresis exhibited by simple triode generators was discussed theoretically. A practical method of reception in which this phenomenon is utilised in a periodic manner was described. This method, which for convenience may be termed "periodic trigger reception," is

suitable for continuous-wave and spark signals.

A low-frequency electromotive force is introduced in the grid circuit of a simple triode oscillator in such a way that high-frequency oscillations are not produced in the absence of an incoming signal. A small signal of high frequency is, however, sufficient to produce a train of free oscillations once every low-frequency cycle. Such free oscillations are rectified by the triode, and a signal of the impressed low frequency is heard in the receiver telephones.

The system differs fundamentally from the Armstrong super-regenerative receiver in the following respects:—

(a) The ordinary oscillation-hysteresis characteristic is followed "adiabatically";

(b) No self-oscillations are produced in the system in the absence of an incoming signal; and

(c) The amplitude of the telephone signal is practically independent of the amplitude of the incoming signal and not proportional to it as in super-regenerative receivers.

It has been discovered experimentally that oscillations may be maintained in a simple triode generator with extreme negative grid potentials such as would cut off the anode current entirely under normal conditions. A simple theory for the conditions necessary for such maintenance is given. An oscillator of this type is very efficient in that anode and grid currents are only permitted to flow for a very small part of the cycle.

*A Dynamic Model of a Valve and Oscillating Circuit*, by R. C. CLINKER, Member.

A mechanical model was described which represented the action of a 3-electrode valve when coupled to an oscillatory circuit. A string-moving around pulleys, one of which is driven by a small motor, represents by its motion the current through the valve. The oscillatory circuit is represented by a spring and a weighted pulley. By a mechanical coupling between the spring and a brake on the driving motor, the effect of the intermittent current through the valve is obtained, and the system exhibits self-maintained oscillations.

#### THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

ORDINARY MEETING.

Held at the Chemical Society's Rooms

on Wednesday, November 7, Mr. P. A. Ellis Richards, President, in the chair.

Certificates were read for the first time in favour of: Mr. Robert Charles Frederick and Hubert Thomas Stanley Britton, M.Sc. (Lond.), F.I.C.

Certificates were read for the second time in favour of: Messrs. Laurence Eversley Campbell, M.Sc. (Lond.), F.I.C.; John Troubridge Hadden, B.A. (Cantab.), A.R.-C.Sc., A.I.C.; Cyril Langley Hinton, F.I.C.; Douglas William Kent-Jones, B.Sc. (Lond.), F.I.C.; Thomas William Alan Shaw, M.Sc. (Liv.); William Hall Simmons, A.I.C.; Kenneth Edward Nethercoate Williams; Percy Noel Williams, M.Sc. (Liv.), A.I.C.

The following papers were read:—

*The Gold-Beaters' Skin Test for Tannins*, by PHYLLIS H. PRICE, B.Sc.

Tanning consists in the fixation of the tannins by animal fibre. A reliable tannin test must therefore demonstrate this specific property, and such a test was described from Dr. Nierenstein's laboratory by Miss E. Atkinson and Miss E. O. Hazleton (*Bio. Chem. Journ.*, 1922, XVI., 516). Their method consisted in the fixing of the tannin on gold-beater's skin and the subsequent staining of the skin with ferric chloride. Non-tannins are not fixed on the gold-beater's skin and consequently not stained. The author has further developed the test, and finds that it is possible to detect 0.00005 gm. of gallotannin in 1 cc. of solution with the use of either ferrous sulphate, ferrous chloride or amyl nitrite fumes in place of ferric chloride. It was also noticed that on decolorisation with dilute hydrochloric acid, skins previously treated with pyrogallol tannins are completely decolorised, whereas those treated with catechol tannins have a reddish stain left on them. This is suggested as a test for Phlobaphenes.

*Determination of Nitrogen in Coal*, by W. DONOVAN, M.Sc.

The author confirms the work of Fieldner and Taylor, Terrea, Fleischer, and others, who observed that the Dumas process, as described in the report of Research Committee of the Institute of Gas Engineers, and the Kjeldahl method both gave results below the correct one, the former owing to incomplete combustion, the latter by loss of gaseous nitrogen, but points out that the

Dumas process makes no provision for the complete removal of hydrocarbons. Concordant results are, however, obtained with the Dumas process (hydrocarbons having been completely removed) by the addition of a constant 0.2 per cent. to the Kjeldahl gure, using mercury as a catalyst.

*The Estimation of Lead in Potable Waters and in Urine*, by JOHN C. THRESH, M.D., D.Sc., F.I.C.

In estimating traces of lead in coloured moorland waters the influence of the colour is not always removed by making the standards with the same water diluted with distilled water. The presence of even one part of copper in 100 millions reduces the depth of the tint given by lead, and iron in solution also interferes with the colorimetric estimation of lead, and accounts for most of the discrepancies obtained with moorland waters. It is essential that the standard should have the same acidity and contain the same acid as the water or urine under examination. A sensitive method of testing for lead in urine is described, and it is shown that three kinds of filter paper contained sufficient lead to cause urine which was free from lead to give a positive result in the test.

#### THE INSTITUTION OF ELECTRICAL ENGINEERS.

A paper, entitled, *The Electrification of the French Midi Railway*, was read by MON. A. BACHELLERY, Ingénieur-en-Chef, Chemins de Fer du Midi, France, and discussed at a joint meeting of the Institution of Electrical Engineers and the Société des Ingénieurs Civils de France (British Section), held on Thursday, November 22.

After a brief description of the experiments made before the war on the Midi Railway in the way of electric traction, the author gives an account of the extensive electrification work now pursued by that company in accordance with the new standard regulations of the French Government, and of the first results already obtained on the electrified lines.

#### LECTURES IN CHEMISTRY.

A course of three lectures on *Some Chapters in the Recent Development of the Theory of Electrolytic Dissociation* will be

given at University College, London (Gower Street, W.C.1), by PROF. J. N. BRONSTED (Professor of Chemistry in the University of Copenhagen), at 5.30 p.m. on Monday, Dec. 10, Wednesday, Dec. 12, and Friday, Dec. 14.

At the first lecture the chair will be taken by Professor F. G. DONNAN, C.B.E., F.R.S.

The lectures are addressed to advanced students of the University and to others interested in the subject. Admission is free, without ticket.

#### WHAT CHEMISTRY SHALL BE TAUGHT IN HIGH SCHOOL AND HOW IT SHALL BE CORRELATED WITH COLLEGE CHEMISTRY.

BY LOUIS W. MATERN.

*Chemical Department McKinley Technical High School, Washington, D.C.*

(Abridged from the "School Science and Mathematics," Vol. XXIII., No. 7, October, 1923.)

No endeavours are so prolific of far-reaching benefits to the betterment of mankind as those which contribute to the aim of education, as expressed by William C. Ruediger, "To educate a person, means to adjust him to those elements of his environment that are of concern in modern life, and to develop, organise and train his powers so that he may make efficient and proper use of them." What a fine instrument chemistry may become as a contributor to develop and to carry out the two aspects of life as implied in that definition, first the objective, and second the subjective.

Objectively, first, chemical principles touch our every day physical environment at every turn in life with an illumination that reveals its indispensable usefulness in manufacturing processes, in furnishing the basic supplies of mankind through agriculture, in the rapid developments of foods and medicine, and in that proper understanding of certain phenomena and substances which is essential to their best usage in connection with personal welfare.

With regard to the subjective aspect, the qualities needed in the study of chemistry and therefore to be accordingly developed in the student, are those which operate prominently in the production of success in modern life, namely, accuracy in observation, correlation of observations and the de-

duction therefrom of principles or laws and the relation of new observations to these laws, independent judgment based on experimental evidence, the ability to check thought and imagination with experimental evidence, the indispensable virtue of thoroughness, and the very important matter of expressing clearly, either written or oral, experimental work.

Subsequent to the great developments of the possibilities of chemistry due to the urge of the researches of Black (1728-99), Cavendish (1731-1810), Priestley (1733-1804), and Lavoisier (1743-94), those interested in education not only gave chemistry a place in the colleges as early as 1767-1839, but also, later on, in the American Academy, which was developed out of a desire to do the people at large more good than the then existing Latin grammar school. At this time a new spirit in American education was struggling for birth. The American spirit in education, animated by such spirits as Benjamin Franklin, William Penn, Rensselaer, Lawrence of Harvard, Williams of Michigan, and Pugh, the first President of the Pennsylvania State College, the blacksmith apprentice, who managed to get enough elementary education to spend four years abroad, returning as an accomplished educator in agricultural science, and others—all brought science to bear upon the welfare of the people at large, both from a practical and cultural point of view. Pugh states, "The facts of science discipline the mind to habits of thought and enable one fully to comprehend the abstract principles involved in the practical operations of life." From 1819 to 1840 in North Carolina, Massachusetts, Connecticut and New York alone, thirty-five academies and secondary schools taught chemistry. It is, therefore, not surprising that the increased revelations of the wonderful possibilities of chemistry since those early days caused a large number of students in the high schools of this country to study chemistry.

This increasingly large number of chemical students is a very important field of chemical education: first, because students in high schools are especially sensitive to visions of their life's work and a long list see chemistry; second, they have the ability to successfully learn chemistry when there is not an attempt to put a quart in a pint measure—remembering that the rest of the quart can better be administered at college; third, the large number whose formal education ceases with the high school carry

into citizenship that which will be helpful in creating more of an intelligent appreciation at large of the importance of chemistry and the value of its many current publications to the material well-being and benefit of mankind.

The problem of correlating the chemistry taught in high schools with college chemistry is a doubly complex problem. The college professors of chemistry receive from high schools those who have had chemistry and those who have not. The high school teachers of chemistry have in their classes those who intend to go to college and those who do not. Different high schools treat chemistry differently, both as to content and method of teaching, thus presenting to the colleges a variety of preparation. Since chemistry may logically play an increasingly important part in high school education, should not the American Chemical Society, with its rich knowledge of chemistry, and its wealth of educational ability, help to solve the problem of how and what chemistry should be taught in the high schools?

How chemistry is taught during the highly sensitive period of high school education, as well as what is taught, is exceedingly important, because the habits and attitude of mind then formed will help mightily to determine the extent of further development in college chemistry. I, therefore, suggest the following method and content for high school students of chemistry, either for those not going to college or those who do; however, the latter is the class for special consideration at this time.

Stress the development of accuracy in observation, without which there can be no real progress in chemistry. Robert E. Rose, in discussing the weakness of chemists, lays particular emphasis on a positive need for more training of the ability to observe accurately, and ascribes a lack of that ability to "faults of our secondary schools." The wide variation of materials and their actions afforded by a properly systemised series of elementary chemistry experiments give an unparalleled opportunity for training of the power to observe.

Student laboratory experiments should precede class-room development, thereby getting information, not second-hand, but first-hand, which arouses curiosity and stimulates keen observation. These observations should become the basis of class-room development and further expansion of the principles taught by these experiments

into their applications in every-day life. In the admirable "Report" of the Committee, appointed by the Prime Minister to inquire into the "Position of Natural Science in the Educational System of Great Britain," attention is properly called to the danger of carrying the heuristic method to an extreme; that is, to discover things through their experiments, with very little aid from their teacher. While the spirit of inquiry should saturate every experiment, it would be a waste of time to compel the students to rediscover all that they are expected to know during the limited time given to laboratory work.

(To be continued.)

### GENERAL NOTES.

#### ANGLO-SWISS TRADE IN 1922.

The Department of Overseas Trade has received from the British Legation at Berne the following survey of Anglo-Swiss trade during 1922.

According to the recently published Customs Statistics for the entire twelve months of 1922, Great Britain maintains her position as Switzerland's chief customer, France coming next, then the United States of America, and then Germany.

According to the *Swiss Exporter* for October, the favourable marketing conditions for Swiss artificial silk are causing the "Viseose S.A." of Emmenbrücke (Lucerne) to contemplate the erection of a second factory in this country. Moreover, a new undertaking for the manufacture of artificial silk is about to be established at Steckborn, by the "Borvisk" Artificial Silk Works, Ltd., of Zürich.

With regard to exports of chemicals, the increase of 10.1 million francs can be attributed almost entirely to aniline and other coal tar dyes. There is also a slight increase in these particular chemical exports, as compared with 1921 (13.1 as against 10.6 million francs), whereas there is a decrease to be noted in respect of the aggregate total of chemicals exported to the United Kingdom. This decrease applies more particularly to perfumery, cosmetics, and vegetable alkaloids. There is a notable increase in exports of technical oils and fats, which have risen from 10.7 million francs in 1921 to 58.5 million francs in 1922.

### CORRESPONDENCE.

#### BRITISH EMPIRE EXHIBITION (1924).

To the Editors of THE CHEMICAL NEWS.

SIRS,—It is well known to most people that at the forthcoming Exhibition next year at Wembley there will be shown a very complete representation of our present state of knowledge of natural science. The details of the arrangements, perhaps, are not so well known, and with a view to furnishing information to those already interested and possibly enlisting the assistance of those who have not already offered it, I shall be glad to be allowed to make the following statement:—

A Committee of the Royal Society is dealing with an exhibit illustrating, so far as space permits, researches in various branches of pure science other than Chemistry.

The Chemistry Exhibit is being organised by a Committee of representatives of all the other scientific societies dealing with science and application of chemistry. The two Committees are working in the closest possible co-operation, having three members in common in order to prevent overlapping.

The space at the disposal of the Committees is limited, but those who are able and willing to assist in the Chemistry Exhibit should communicate with Dr. Levinstein, at 166, Piccadilly, W.1, or any of the Convenors of Sections, whose names are given below, with regard to exhibits dealing with chemistry.

Subjects which are on the borderland of Physics and Chemistry, such as the Structure of the Atom, the Inner Structure of Crystals, and recent Spectroscopic work, will be dealt with by the Committee to which it is most appropriately referred. Arrangements will be made between the two Committees to exhibit the work in its most appropriate place.

#### CHEMISTRY EXHIBIT.—CONVENORS:

Dr. E. F. Armstrong, F.R.S., Greenback, Letchford, Warrington; Catalysis: Fat, Hydrogenation of.

J. L. Baker, Esq., F.I.C., Dial Cottage, Cookham Road, Maidenhead; Biochemistry.

Professor E. C. Baly, C.B.E., M.Sc., F.R.S., The University, Liverpool; General Inorganic.

A. Chaston Chapman, Esq., F.R.S., 8, Duke Street, Aldgate, E.C.3; Hydrogen Ion Concentration.

C. F. Cross, Esq., B.Sc., F.R.S., 4, New

Court, Lincoln's Inn, W.C.2; Cellulose.

Professor F. G. Donnan, C.B.E., F.R.S., University College, Gower Street, W.C.1; General Physical Chemistry.

Professor G. G. Henderson, LL.D., F.P.S., The University, Glasgow; Terpenes.

Dr. T. A. Henry, The Wellcome Chemical Research Laboratory, 6, King Street, Snow Hill, E.C.1; Organic Chemistry Alkaloids.

Professor I. M. Heilbron, D.S.O., Chemistry Department, The University, Liverpool; Plant Colouring Matters.

Dr. J. T. Hewitt, F.R.S., Manor House, Sutton, Heston, Hounslow, Middlesex; Coal Tar Colouring Matters.

Professor J. W. Hinchley, A.R.S.M., F.I.C., The Institution of Chemical Engineers, N.307, Abbey House, Victoria St., Westminster, S.W.1; Chemical Engineering.

Principal J. W. Irvine, C.B.E., F.R.S., The University House, St. Andrews, Fife; Sugars.

Dr. Arthur Lapworth, D.Sc., F.R.S., The University, Manchester; Valency Theories and Theories of Chemical Combination.

Professor J. W. McBain, M.A., F.R.S., The University, Bristol; Colloids.

Sir Henry Miers, LL.D., F.R.S., Birch Heys, Cromwell Range, Fallowfield, Manchester; Crystallography and Crystal Structure.

Dr. W. R. Ormandy, F.I.C., 18, Belsize Grove, Belsize Park, N.W.3; Plastics.

Professor F. L. Pyman, D.Sc., F.R.S., College of Technology, Manchester; Alkaloids.

R. B. Pilcher, Esq., O.B.E., The Institute of Chemistry, 30, Russell Square, W.C.1; Historical.

Sir John Russell, D.Sc., F.R.S., Lawes Agricultural Trust, Rothamstead Experimental Station, Harpenden; Agricultural Chemistry.

Dr. T. Slater Price, O.B.E., F.I.C., British Photographic Research Association, 30, Russell Square, W.C.1; Photography.

Professor A. Smithells, C.M.G., B.Sc., F.R.S., 68, Lissenden Mansions, Highgate Road, N.W.8; Flame, Fuel and Explosion Waves.

Commander R. E. Stokes-Rees, R.N., The Institution of Petroleum Technologists, 5, John Street, Adelphi, W.C.1; Apparatus.

Professor J. F. Thorpe, G.B.E., F.R.S., The Imperial College of Science and Technology, South Kensington, S.W.7; General Organic Chemistry.

The next meeting of the Committee is to be held on December 19, and it is hoped that prior to this date sufficient information will be in the hands of each Convenor to enable him to make a close estimate of the amount of space he will require and the expenses which will be incurred in his section. It is essential that this date be adhered to, if the subsequent work is to be efficiently carried out.

The idea of having standard specimen bottles has been abandoned, and specimens will be shown in exhibitors' own bottles, except in special circumstances. The importance of the Scientific Exhibits has already been well recognised by the technical press, and I am, therefore, encouraged to hope that the widest publicity may be given to the details of the arrangements which have already been made.—Yours, &c.,

W. J. V. WOOLCOCK.

*The Association of British Chemical Manufacturers.*

166, Piccadilly, London, W.1.

November 21, 1923.

#### RED SULPHIDE DYES.

*To the Editors of THE CHEMICAL NEWS.*

SIRS,—In a recent paper communicated to this Journal on the subject of sulphur dyes, the author remarked that sulphide dyes are known in every colour but red (*The Chemical News*, 1923, CXXVII.). The recent research of Watson and Dutt on the subject of these dyes deserves, in view of this, some mention. The first paper on this subject communicated to *The Chemical Society* in 1922, expressed the view that the lack of fastness of these dyes was due to the fact that they contained ordinary auxochromes, such as amino or hydroxyl groups, as well as mercaptan groups, and the presence of these ordinary auxochromes caused the dyeings to be stripped to a certain extent by acids or alkalis. Some substances were therefore prepared containing chromophores and mercaptan groups, but no auxochromes. Thus 4 benzeneacinaaphthylmercaptan was found to be soluble in sodium sulphide, but only to dye in light brownish shades. Despite this it was hoped that the mercaptan derivatives of the various groups might prove more valuable red sulphide dyes than the compounds prepared by various previous workers. But the various new compounds of the azine, oxazine, phthalein, nitroso and acridine groups all failed for one reason or another. Thus 2-amino-8-thiol-10-phenyl phenazonium hydroxide,

though a sulphide dye, was found to dye only in dull violet shades; 3-amino-7-dimethylamino-4-thiophenazine only to give red-brown shades very sensitive to acids an dalkalis; 9-dimethylamino-2-thiol-3-phenoxazone to be soluble in sodium sulphide, but only to give blue shades. The following compounds were prepared:—

Ethyl 4 Benzeneazo 1 naphthyl xanthate,  
4 Benzeneazo 1 naphthyl mercaptan,  
pp'p" trithioltriphenylcarbinol,  
2 amino 8 thiol 10 phenylphenazonium  
hydroxide,  
3 Amino 7 dimethylamino 4 thiolphenazine,  
9 Dimethylamino 2 thiol 3 phenoxazone,  
Dithiofluorescein,  
Dinitrosothioresceinol, and  
2:2':4:4' Tetra amino 5:5' dithioldi-  
phenylmethane.

Yours, &c.,

R. F. HUNTER, F.C.S.

Highbury, N.E.

#### NOTICES OF BOOKS.

*Recent Developments in Atomic Theory*, by LEO GRAETZ (Professor of Physics in the University of Munich), Translated from the German by G. BARR. Pp. XI. + 174 (with index). 1923. Messrs. Methuen & Co., Ltd., 36, Essex Street, W.C.2. 9s. net.

This is a welcome book, coming just at the time when so much interest is developing in connection with atomic theories.

The book opens on somewhat conventional lines, dealing with molecules and atoms. In passing we notice the statement that "Molecules are the units of structure of compounds." This is really only a half truth, and there are several such half truths noticeable in the book. It has been experimentally demonstrated that in certain crystals, for example, the atom or molecule loses its identity, so that the attempt to sub-divide all matter by hard and fast degrees breaks down in this type of case.

The book is, however, strong on the physical, or more particularly the electrical, side, and the chapter on atoms and ions is excellent.

The usual statement that Helmholtz (1881) was the first to draw important conclusions from Faraday's experiments involving the conception of atomic or molecular electricity, appears in this book; but some time prior to 1881 the idea of molecular electricity was known. Still we do

not wish in any way to minimise the value of Helmholtz's suggestions.

The statement appears on p. 29 that "electricity behaves like a special chemical element, whose atoms combine with those of the other known elements to form ions." Hydrogen without its electron would be an ion, so that this statement is again in the nature of a half truth according to recent views. These should be corrected in the second edition.

Disintegration of atoms, X-ray spectra, line spectra, Bohr's model, and the "decomposition" of nuclei are dealt with clearly.

Balmer's law is represented in a very clear manner, which points to the desirability of physicists making their equations attractive in appearance to the lay mind and also businesslike for quick appreciation.

The table of isotopes on p. 88, head of third column, should read II. The system of closed branching, see p. 65, as is used in Germany, is adopted, notwithstanding the International Committee's Report.

The usual error of tacitly accrediting Aston with the discovery of the two neon isotopes is made in this book. As a matter of fact, Sir J. J. Thomson was the first definitely to isolate the component isotopes of neon by means of his positive rays; but we have few impartial historians in science as yet.

The book is well illustrated, while the translator is to be congratulated on the lucidity of his style.

*The A.B.C. of Atoms*, by BERTRAND RUSSELL, F.R.S. Pp. 175 (no index). 1923. Messrs. George Routledge & Sons, Ltd., Broadway House, 68-74, Carter Lane, E.C.4. 4s. 6d. net.

This little book, as a popular exposition of the atom, is well worth perusal by all interested in the subject, but there are some statements which should be corrected in the second edition. For example, on page 13, the end-product of disintegration is referred to as a lead "of a sort." As we all know, it is lead in every sense of the chemical and physical meaning we attach to common lead. On page 62 it is stated that the atom has least energy when the orbit is smallest. This does not necessarily follow. What energy the electron retains, and what energy the electron absorbs and gives out are two quantities that should not be confused with each other. On p. 129 the following appears: "When two elements have the same atomic number they are

called 'isotopes.' " Chlorine 35 and chlorine 37 have the common atomic number 17, but isotope 35 is not one element and isotope 37 another. The word element in this case embraces all atoms, whatever their difference in atomic weight may be. The above statement was made in connection with radio-activity, when two differently-named elements may be isotopically alike, but such statements are not satisfactory.

The book, however, abounds in many happy statements, and it should have a wide circle of readers. The absence of the usual diagrams and an index are a disadvantage to a book of this kind.

#### BOOKS RECEIVED.

*Industrial Filtration*, by ARTHUR WRIGHT, M.E. Pp. X. + 336. Vol. I., 1923. The Chemical Catalog Co., Inc., 19, East 24th Street, New York, U.S.A. \$5.00.

*Kolloide in der-Technik*, von DR. RAPHAEL ED. LIESEGANG. Pp. 157. 1923. Herr Theodor Steinkopff, Residenzstrasse 12b, Dresden and Leipzig. 3s. 6d.



This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

- 28156—Bachalard, G.—Preparation of sulphuric anhydride. Nov. 8.  
 17804—Coppee, E.—Manufacture of pure alcohol. Nov. 5.  
 28008—Dreyfus, H.—Manufacture of cellulose derivatives. Nov. 7.  
 2774—Koppers Co.—Manufacture of alkali sulphides from thiosulphates. Nov. 5.  
*Specification Published this Week.*  
 195345—Holzverkohlungs-Industrie Akt-Ges.—Process for the chlorination of methane.  
*Abstract Published this Week.*  
 204223—Lead arsenate.—McDougall, I., of 66, Port Street, and Howles, F., of Glenluce, Water Park Road, Broughton Park, both in Manchester.

Lead arsenate is obtained by reacting with arsenic acid upon a colloidal solution of lead oxide in water, aqueous solution, or other suitable dispersion medium, preferably at a raised temperature. The arsenate precipitates in a finely divided form. An example describes the production of the arsenate  $PbHASO_4$  in this manner, the colloidalising of the lead oxide in water being effected in a Plauson mill, steam being passed through the jacket of the mill so as to raise the temperature to  $80-100^\circ C$ . The arsenic acid is run into the mill and the reaction is effected in a few minutes.

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# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3221.

## THE SEPARATION OF HAFNIUM FROM ZIRCONIUM.

By G. HEVESY AND V. THAL JANTZEN.

In the issue of *The Chemical News* dated July 20, 1923 (Vol. CXXVII., p. 33), a short account of the methods generally used in the separation of hafnium from zirconium was given. We have received requests from different sources to give a more complete account of our experimental work, and of the efficiency of the methods employed. In deference to these requests we propose to give, in the present paper, a detailed description of the preparation of hafnium by the double fluoride method.

When working with larger amounts of minerals, we abandoned the method originally used, of preparing and crystallising the potassium zirconium fluoride. Under such conditions the method of crystallisation of the corresponding ammonium salt was found more suitable. This compound possesses a solubility<sup>1</sup> about ten times as large as that of the potassium salt. Moreover, it is very stable, it can be crystallised out in

porcelain dishes without these showing any indication of having been attacked, and it crystallises in beautiful crystals.

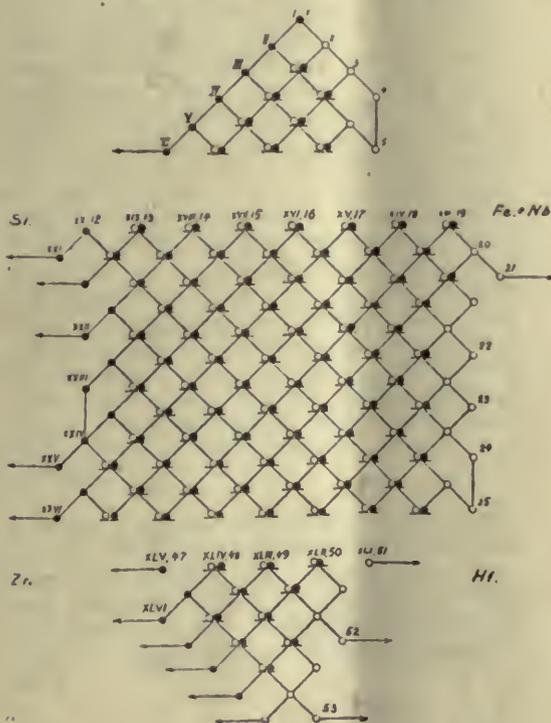
To prepare this compound, the pulverised mineral is first treated with hot concentrated hydrochloric acid, to remove the iron and other soluble impurities present, and the mineral which has been thus purified is then mixed in small portions with fused acid ammonium fluoride in a large platinum crucible.

Using the zirconium mineral alvite, it was found that a part of its zirconium and hafnium content is soluble in concentrated hydrochloric acid. In view of this, the preparation of the double salt of ammonium was carried out in two parts: (a) The fraction insoluble in hydrochloric acid was fused with about four times its weight of acid ammonium fluoride; (b) the hydrochloric acid solution was evaporated to dryness to render the silica insoluble, and the  $ZrOCl_2 + HfOCl_2$  was extracted with cold water, purified from iron and other impurities by crystallisation, and converted into ammonium zirconium and ammonium hafnium fluorides respectively.

In what follows, we shall give a detailed description of the treatment of the portion (a).

After the mineral has been fused with acid ammonium fluoride, it is extracted repeatedly with boiling water, which dissolves zirconium, hafnium, titanium, niobium, tantalum, vanadium, germanium, iron, and manganese, some of which are present only in very minute quantities, and very considerable amounts of ammonium silicon fluoride. Thorium, the higher homologue of hafnium, and also the rare earth elements present, remain insoluble, together with unattacked mineral and insoluble zirconium and hafnium fluoride compounds, such as sodium zirconium fluoride.

On cooling down the solution, denoted in the diagram by I.1, the greatest part of the double fluorides crystallises, supplying the crystals indicated by II.1, and a mother liquor I.2. The next step consists in dissolving II.1 in boiling water, from which, on cooling, the crystals III.1 and the mother liquor II.2, are obtained. The mother liquor I.2 is now partly evaporated, and on cooling it supplies the crystals II.2, together with the mother liquor I.3. The mother liquor II.2 is used to dissolve the crystals II.2. The successive steps in the crystallisation are indicated in the following diagram, the black dots representing crystals and the circles mother liquors:—



## DESCRIPTIVE TABLE OF CRYSTALS REMOVED.

Fraction.	Total Weight of Double Fluorides.	% of ZrO <sub>2</sub> .	% of HfO <sub>2</sub> in ZrO <sub>2</sub>
VI,1	848	0.5	0.5
VIII,2	415		
XIII,4	310		
XVI,6	190		
XVII,7	120		
XVII,8	165	1.6	2.5
XVIII,9	134		
XXI,12	117		
XXI,13	198		
XXII,14	101		
XXV,16	91	11.2	<2
XXVI,17	54		
XXVI,18	84		
XXVII,19	35		
XXVIII,20	35	13	
XXIX,21	39		
XXIX,22	56		
XXX,23	79		
XXXI,24	130		
XXXII,25	124	36	<2
XXXIII,26	88		
XXXIV,27	93		
XXXV,28	74		
XXXV,29	90	c.50	<2
XXXVI,30	45		
XXXVI,31	97		
XXXVII,32	41		<2
XXXVIII,33	32		
XXXVIII,34	33		
XXXVIII,35	42		
XXXVIII,36	56		<2
XXXVIII,37	98		
XXXIX,38	25		
XXXIX,39	25		
XXXIX,40	40		3
XL,41	12.4		
XLI,42	21.4		
XLI,43	13.2		2
XLII,44	14.2		
XLIII,45	7.6		9
XLIV,46	6.5		
XLV,47	14.4		15
XLVI,48	12.2		
XLVI,49	15.9		25
XLVI,50	12.1		
XLVI,51	13.4		35
XLVI,52	15.9		

The results of crystallisation were checked by first determining the sum-total of zirconium, plus hafnium, plus traces of impurity present. This was performed by weighing the oxides obtained by treatment of the double fluoride with concentrated sulphuric acid, and igniting. On the other hand, the hafnium content was determined by using the methods of quantitative X-ray spectroscopy, as described by D. Coster in *The Chemical News*, dated August 3, 1923 (CXXVII., pp. 65-70).

As shown in the accompanying table, fractions first removed contained practically only ammonium silicon fluoride. As we proceed downwards in the table, the amount of this compound diminished, and the fraction XXXV/29 is practically pure zirconium salt, with about 2 per cent. hafnium content.

Not until fraction XLIII/45 has been reached does the hafnium content begin to increase in the removed crystal fractions considerably; this fraction contains 9 per cent. of hafnium.

Whereas the major part of the crystal fractions obtained by the process described was found to be practically free from hafnium, the bulk of the hafnium was present in high concentration in the mother liquors. The fraction of these which was first removed from the system was V.11. It consisted chiefly of highly soluble impurities such as the double fluorides of iron, manganese and niobium, and about 4 to 5 per cent. of hafnium salt. Fraction XIII/21 still contained about 10 per cent. of impurities, 20 per cent. of  $ZrO_2$ , and 70 per cent. of  $HfO_2$ . On the other hand, fraction XXXVI/48 revealed a hafnium content of about 99 per cent., a zirconium content of not more than 1 per cent., traces of titanium, niobium and manganese, and very minute traces of vanadium and germanium. The existence of the elements present only in traces was detected by optical spectroscopy. Fraction XLI/51 contained 97.5 per cent., fraction XLIII/53 95 per cent., of hafnium.

When a mixture of hafnium and niobium double fluorides is heated carefully, and afterwards treated with boiling water and acid ammonium fluoride, only the hafnium salt dissolves. This method was repeatedly used to remove niobium from our preparations.

The elaborate work of 650 crystallisations was performed in order to extract in a concentrated form the major part of the hafnium present in the mineral.

<sup>1</sup> We propose to give a detailed account of the solubility measurements in a subsequent issue of "*The Chemical News*."

*Institute of Theoretical Physics,  
Copenhagen University.  
September, 1923.*

## ARE THE NATURAL GROUPINGS OF THE ELEMENTS AND THE SPECTRAL LINES OF HYDROGEN RELATED?

PART V.

BY F. H. LORING.

In developing this study—see *The Chemical News*, 1923 CXXVII., pp. 225, 257, 273, 290, 337—some further interesting features are brought into consideration; but before making deductions therefrom it will be necessary to acquaint the reader with a line of research of very considerable scientific importance. Moreover, the digressions here made have a direct bearing on the argument, and give support to it, as will be seen presently.

Prof. L. Vegard, in the *Philosophical Magazine* for October, 1923, contributes a paper entitled "The Constitution of the Upper Strata of the Atmosphere," in which he propounds a theory, based upon experiment, that in the higher regions of the earth's atmosphere, where the aurora curtain phenomenon is confined, clusters of nitrogen molecules, forming a sort of dust (crystals), exist.

It is, moreover, suggested that this dust is carried upwards and maintained at high atmospheric levels by reason of the electrically charged state of the particles, and that this charged state is due to a photo-electric effect arising from the incident rays, including ultra-violet light, of the sun. It will be remembered that ultra-violet light falling on substances causes the emission of electrons therefrom, leaving the substance positively charged. In this case, however, corpuscular rays from the sun may be involved, and, indeed, the magnetic field of the earth plays a part in these phenomena, and consequently the aurora is locally produced. The negative electric charge of the earth is supposed also to influence the auroral displays.

The spectrum lines of the aurora, in particular the famous green line, occurring at the altitudes within which this phenomena

is observed, and a certain agreement between this spectrum and that of normal nitrogen, is advanced as good evidence that the aurora is due to the sun's rays impinging upon *solid* nitrogen particles. Electron rays are mentioned in this connection.

Prof. Vegard further suggests that it is these particles which give rise to optical scattering, so that the sky is rendered blue by reflected light. The twinkling observed in the case of fixed stars is attributed to the same fundamental cause. Prof. Vegard's paper is summarised at the conclusion of this section.

Of immediate interest to the present argument, however, is Vegard's view that the bending of Hertz waves so that they conform to the general curvature of the earth is due to the state of affairs arising from the layer of charged nitrogen crystals surrounding the earth as a dust layer situated at a high altitude.

The problem of the bending or reflecting downwards of the electric waves has been under discussion for many years; and Prof. Fessenden and Dr. Elihu Thomson have contributed towards its solution, the former supporting the view that at high altitudes, beginning at the lower termination of the auroral draperies, there were ionised gas particles, this ionisation being induced by direct rays from the sun; while the latter advocated a gliding theory, the waves being as it were attached to the earth so as to follow its contour, much in the same way as electric waves become attached to conducting wires. The layer of ionised gas, supposed to act as a deflecting medium, has been mathematically studied by Professors Fleming, Eccles, and others, this layer being known as the Heaviside layer owing to Heaviside's mathematical work in general in connection with such matters.

Thus it will be seen that there are three theories involved in the elucidation of this phenomenon, which arose from researches in connection with wireless work. These may be referred to as (1) *the gliding theory*, (2) *the ionised gas Heaviside layer theory*, (3) *the nitrogen crystals Heaviside layer theory*.

Now, Prof. Vegard shows that the gas theory is untenable; that is to say, ionised gas will not account for the spectrum obtained, and it is therefore supposed that the bombardment of the nitrogen crystals by corpuscular rays from the sun will account for the peculiarity of the spectrum of the

aurora draperies observed at the lower edge and at the highest region.

It frequently happens that when theories are first established, there are phenomena involved which coincide in their effects so that the theory is not the whole truth, but only an overlaid truth, which would become modified when more knowledge is brought to bear upon the subject.

In the case of the Heaviside layer, it is quite possible that the radiation may tend itself to describe what might be termed a ground orbit round the earth. This idea is made possible from the following considerations: In Parts I. and II. of this paper it has been shown that the first five Balmer emission lines of the hydrogen atom are linearly related to five natural groups and groupings of the elements in the periodic table; and in Part III. of this series, that these same values are in close agreement with the spacing of five consecutive planets (regarding the asteroids as collectively one planet); and in Part IV., also of this series, that the many-lines spectrum of the hydrogen molecule accords very well in its intensity distribution with the distribution of the asteroids.

To be able to pass in this manner from the smallest known phenomenon to one on the huge scale of the planetary system seems to involve a *place principle* of universal significance, which gives to space round all bodies a controlling feature of its own, quite apart from the mass magnitudes of the outer bodies concerned. If this is true, as seems to be the case, then it is only a natural step to consider whether radiation will not, under suitable conditions, describe closed orbits round bodies including atomic nuclei. This is, of course, a new idea as applied to the atom, as it had been supposed that radiation could only travel in straight lines through space, though Einstein's theory shows that light from the stars is slightly bent in its course past the sun, and Hertz-wave experiments seem to show bending round bodies. Just what the conditions are is, of course, speculation, but the strong fields round atoms, or rather round atomic nuclei, and presumably also the positively charged particles in the Heaviside layer, may account for the interpretation of the phenomena indicated.

If there is a germ of truth in this idea, then it may be that all the atomic orbits are not due to electrons actually describing them; but that they are described by pure radiation, while the electron as the opera-

tor may only vibrate and pass from one practically fixed radial abode to another, linear or radial radiation being given out when the orbit is broken or detached. The electron, on this view gives rise to the orbital radiation, but to all intents and purposes the electron is stationary, so that the Lewis-Langmuir theory can be retained in its present form with, of course, modifications in detail, as has been made by recent investigators. In the case of the Bohr orbits, these are, on this view, electro-dynamically equivalent to an electron describing such orbits.

Considering the stability of the electron in its stationary position outside the nuclear part of the atom, it is quite possible to regard the electric fields involved as so disposed that the electrons accommodate the most electric lines when they are at places a little distant from the nucleus, just as an iron disc will not remain face down on the flat face of a magnet, for the simple reason that in its upright or edge position it can accommodate more magnetic lines of force. It must be remembered that the lines of electric force in the atom are reduced to their lower numerical limit in joining up with one electron, and on this account something in the nature of a limiting condition must prevail. This is discussed in the writer's "The Chemical Elements," Chapter IX.; see also page 161.

Considering now Planck's radiation theory involving energy quanta, this would not be interpreted in quite the same way as at present, since the quanta would merely be apportionments of closed radiations (orbits), and open radiations, so to speak (see Notes to follow). The closed radiation is atomic or quantum like, while the open radiation behaves in accord with the undulatory theory of light. On this view a model could be constructed showing the various quantum groups emitted as the various orbital-radiations are broken or detached, which would accord with Planck's energy equation. See the writer's "The Chemical Elements," page 82.

#### SUMMARIES.

The Heaviside layer, which is supposed to cause Hertz waves to conform to the general contour of the earth, is discussed in the light of Vegard's theory that the higher regions of the atmosphere contain minute positively charged crystals of nitrogen, but it is suggested that these waves may tend to describe a ground orbit round the earth, because orbital phenomena do not depend upon the mass of the circulating body, as is

evident from the fact that the five Balmer lines of the hydrogen atom are linearly related to the groupings of the elements in the periodic table, to the radial positions of five consecutive planets of the solar system, and the many-lines spectrum of molecular hydrogen is possibly related to the distribution of the asteroids. This leads to the idea that the Bohr orbits are closed-radiation orbits, which only give rise to emission lines when the electron is displaced so as to allow the radiation to expand as a radially-directed wave, which conforms in its behaviour after leaving the atom with the undulatory theory of light. Having thus practically stationary electrons, the Lewis-Langmuir theory may be a true one. The quantum theory is then an apportionment of open and closed radiations, for each closed element of radiation is of the nature of a quantum. The closed radiation being mathematically equivalent to a moving electron, while the electron may only vibrate. Is it not possible for the laws established by Bohr and others to be retained with only a slight alteration in their interpretation, as will be seen by considering the action of a model liberating various closed orbits of radiation which become "linear" or "radial" radiations?

Vegard's summary of his paper follows here. It contains much of general interest.

1.—Photographs of auroral spectra corresponding to different altitudes have been obtained.

2.—The intensity of the green line relative to that of the nitrogen bands does not increase as we pass upwards, but shows a small but noticeable diminution.

3.—The observations show that the green line cannot be due to any light elementary gas, such as H, He, or the hypothetical geocoronium.

4.—The green line must originate from nitrogen or from some substance attached in some way to nitrogen. Arguments are given for considering the latter possibility to be excluded.

5.—Independent of any hypothesis with regard to the origin of the green line, observations show that nitrogen is a prominent component of the atmosphere to its very upper limits.

6.—To explain this fact we must either assume for the auroral region an increasing temperature amounting to several hundred degrees centigrade, or we must assume that nitrogen is kept up by the effect of electric forces. Various circumstances seem to exclude the first possibility.

7.—The differential equation for the variation of density in an electrified atmosphere has been found, but its solution has not been carried farther because some simple calculations have shown that a highly electrified upper gas layer cannot exist.

8.—If we adhere to the hypothesis that nitrogen is driven upwards by electric forces we are led to the assumption that the nitrogen in the upper layer is condensed into small crystal particles, which are then electrified through the photo-electric effect of the sun's rays of very short wave-lengths.

9.—The auroral spectrum should be produced when electric rays from the sun penetrate into the layer of nitrogen dust.

10.—The colour changes of the auroræ are explained through disintegration or evaporation of the dust particles caused by the cosmic electric rays.

11.—Our view with regard to the physical state of the atmosphere gives a simple explanation of the following phenomena:—

(a) The sudden change of colours along the track of a meteor.

(b) The increase of the maximum height of auroral rays as we pass towards lower latitudes.

(c) The zodiacal light.

(d) The blue colour of the sky.

(e) The twinkling of fixed stars and the absence of twinkling in the case of planets.

(f) The reflection of electric waves and sound waves from the upper layer of the atmosphere.

(g) The secondary auroral phenomena.

(h) The absence of an upper layer consisting of the light gases, hydrogen and helium.

## INDIGOID DYESTUFFS.

### PART I.

BY R. F. HUNTER, F.C.S.

(Continued from Page 341.)

Bayer's synthesis of 1880 was improved two years later by his synthesis from *o* nitro benzaldehyde. *o*-Nitrobenzaldehyde was condensed with acetone in the presence of alkalis to *o* nitro phenyl lactone methyl ketone. This, on treatment with alkalis, eliminated water and acetic acid passing into indigo. The hydroxy ketone, on dehydration with acetic anhydride, yielded *o* nitro styryl methyl ketone which, with alkalis, gave indigo.

These, however, were not of commercial value, since toluene was the starting material. In 1890 Heumann published a new synthesis of indigo, the starting materials of which were benzene and acetic acid. Aniline was obtained from benzene and monochloroacetic acid from acetic acid, and these were condensed to give phenylglycine. This, on fusion with alkalis at 300° or above, eliminated water, giving indoxyl. This, by atmospheric oxidation, gave indigo, the yield, however, was bad. Three years later accomplished the synthesis in extensive use to-day, *viz.*, the anthranilic acid synthesis. Anthranilic acid condensed with chloroacetic acid yields phenyl glycine *o* carboxylic acid. This, on alkali fusion, gives indoxyl acid, and this, on oxidation, gives indigo. Seven years later the process was being worked on a commercial scale by the Badische anilin and Soda Fabrik. The trouble was, of course, to obtain a suitable source of anthranilic acid; naphthalene provided this. Naphthalene being oxidised to phthalic acid by means of sulphuric acid and mercury, this being converted into its anhydride, and thence to the imide by means of sulphuric acid and mercury, this being converted into its anhydride and thence to the imide by means of ammonia, and this, on treatment with caustic soda and chlorine, giving anthranilic acid. The process of condensation has been recently modified, the acids being condensed in the form of their alkali salts. A still better modification is to treat the sodium salt of anthranilic acid with sodium bisulphite compound of formaldehyde and with sodium cyanide; a nitrite is obtained which hydrolyses to phenyl glycine carboxylic acid.

A synthesis allied to Heumann's consists of condensing aniline with ethylene chlorohydrin and fusing condensation product with caustic soda, the melt, on oxidation, yielding indigo. Another synthesis is by heating glycolide with aniline at 200°, the product being glycollanilide. This, on alkali fusion, gives a mixture of indoxyl and indoxyl acid, and this, on oxidation, yields indigo.

Sandemeyer's synthesis is worthy of note. Aniline is converted into thio carbanilide. This, warmed with KCN and white lead in aqueous alcohol at 60°, yields hydrocyano diphenyl carbimide. This, on treatment with Am<sub>2</sub>S for two days at 30° proceeds to the thioamide. This, with H<sub>2</sub>SO<sub>4</sub> at 110°, gives isatin and anilide. This, on reduction with Am<sub>2</sub>S, yields, firstly, thio isatin, and finally indigo. Another synthesis by the

same author depends on the preparation of isatin anilide by action of concentrated  $H_2SO_4$  on amidine obtained by condensation of aniline and chloroloxime.

Among the other syntheses of indigo, we might mention Nencki's synthesis of indigo by action of ozone on indole. Camp's synthesis from *o* nitro acetophenone. Homolka's preparation from *o* amino aceto phenone, which on heating at  $200^\circ$  with sulphur in a high boiling solvent, eliminated hydrogen as  $H_2S$  giving indigo. Simoni's synthesis from dianilinomaleic acid from aniline and dibromomaleic acid is worthy of note.

Bauer's preparation from oxanilide is likewise of interest, and Reissert prepared indigo in the following way: *o* nitro toluene was condensed with ethyl oxalate in presence of sodium ethoxide to give ethyl *o* nitro phenyl pyruvate, which on reduction gave *N* hydroxy indole carboxylic acid, which he oxidised to indigo. Indole, the starting point of Madelung's preparation, has been synthesised in a number of ways. *o* nitro *w* chloro styrene obtained by bleaching powder on *o* nitro cinnamic acid is reduced to aminochloro compound. This, on heating with sodium ethoxide, gives indole: *o* nitro benzaldehyde can be converted into *o* aminobenzaldehyde, this to *o* aminobenzaloxime, and this to corresponding *o* aldehyde glycine; this is converted into indole by ring closure brought about by heating first with acetic anhydride and anhydrous sodium acetate, and then with aqueous alkalis.

Indole treated with amyl nitrite and sodium ethoxide gives isonitroso indole. This can be reduced to aminoindole, this oxidised to indigo doimine, and this hydrolysed by boiling  $HCl$  to indigo.

It is now proposed to deal with some of the derivatives and analogues of indigo, and it is further proposed to use the classification used by Thorpe and Ingold in their recent work on Vat Dyestuffs. The first group of compounds to be considered are the halogen derivatives of indigo. The following compounds have been described:

- 5 Monochloro indigo;
- 5:5' dichloro indigo;

- 5:7:5' Thichloro indigo;
- 5:7:5':7' Tetrachloro indigo;
- 5 Monobromindigo;
- 5:5' Dibromo indigo;
- 5:7:5' Tribromo indigo;
- 5:7:5':7' Tetra bromo indigo;
- 4:5:7:5':7' Penta bromo indigo;
- 4:5:7:4':5':7' Hexa bromo indigo;
- 5 Chloro 5' bromo indigo;
- 5 Chloro 7:5' dibromo indigo;
- 5 Chloro 7:5':7' tri bromo indigo;
- 5:7:5' Trichloro 7' bromo indigo;
- 4:4' Dibromo indigo;
- 5:5' Dibromo indigo;
- 6:6' Dibromo indigo;
- 7:7' Dibromo indigo;
- 5:7:4:7' Tetra chloro indigo;
- 5:6:5':6' Tetra chloro indigo;
- Octa chloro indigo.
- Octa bromo indigo;
- 5:7 Dibromo indigo;
- 6:6' Dichloro indigo.

The following nitro and amino compounds have been described:—

- 5:5' Diamino indigo;
- 6:6' Dinitro indigo;
- 6:6' Diamino indigo;
- 6:6' Diamino 5:7:5':7' tetra bromo indigo.

Among the sulphonic and carboxylic acid derivatives we might mention:—

- Indigo 5 mono sulphonic acid;
- Indigo 5:5' disulphonic acid;
- Indigo 5:5:7' tri sulphonic acid;
- Indigo 4:4' dicarboxylic acid.

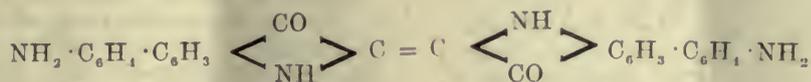
As hydroxy and methoxy derivatives, we have:—

- 4:4' Dichloro 7:7' dihydroxy indigo;
- 4:4':6:6' Tetra chloro 7:7' dehydroxy indigo;
- 5:5' dihydroxy indigo;
- 7:7' Dihydroxy indigo;
- 4:4' Dimethoxy indigo;
- 5:5' Dimethoxy indigo.
- 6:6' Dimethoxy indigo; and the
- 7:7' Dimethoxy indigo.

As homologues of indigo there are:—

- 7:7' Dimethyl indigo;
- $\alpha$  Naphthalene indigo; and
- $\beta$  Naphthalene indigo.

A diphenyl derivative has recently been prepared:—



5:5' Di p amino phenyl indigo.

WHAT CHEMISTRY SHALL BE  
TAUGHT IN HIGH SCHOOL AND HOW  
IT SHALL BE CORRELATED WITH  
COLLEGE CHEMISTRY.

By LOUIS W. MATTERN.

*Chemical Department McKinley Technical  
High School, Washington, D.C.*

(Abridged from the "School Science and  
Mathematics," Vol. XXIII., No. 7, Octo-  
ber, 1923.)

(Continued from Page 349.)

At the very beginning, the high school student in chemistry should be brought in full harmony with the fact that chemistry is guided by fundamental principles, or laws, which find a great variety of material expressions, and is not a mere memorisation of unrelated, isolated facts, and bugbear equations. Professor Remsen's statement to a class of students in chemistry might well be a motto for all high school students in chemistry: "Those who are looking for anything else than a clarification of fundamental principles need not stop here." All experiments should lead to the development of fundamental principles, and their application in experiments having problems to solve, and not merely entertaining tests, revealing no principles nor relationships. Too often, students have been pushed into the applications of chemistry without a knowledge of those fundamental principles of which the applications are but the expressions, and thus in the wild rush to be practical, the very thing that will produce practical results has been omitted. As time permits, many applications should be presented, but always illustrative of fundamental principles. Principles and applications are the combinations that will produce far more interest and permanent benefit than short industrial and applied courses in chemistry without the proper foundation of fundamental principles. George W. Walker, of the Hupp Motor Car Corporation, even goes so far as to state: "For the best training and education of the individual chemist, the first and most important thing is to *forget all about industry*," and, "A student who intends to make a life work of chemistry should study it from the standpoint of a scientist rather than the standpoint of a factory manager."

The chief chemist of one of the leading

scientific chemical commercial laboratories made this statement: "A working knowledge of fundamental principles, rather than routine ability alone, should be emphasised in the training of a successful chemist." William C. Ruediger states: "The person who understands the theory underlying a line of activity can see the reasons for modifications and advances and, having a basis for assimilation, can adjust himself accordingly." I am sure that college professors of chemistry will agree that a firm grasp of certain fundamentals should be given in the chemistry of high schools, because they are essential for the solution of the many important problems in the ever widening field of chemistry.

The ability to make a correct report, either written or oral, of laboratory work, seems like too small a matter to mention at this time, but it is exceedingly important. The high school student in chemistry should possess this ability before continuing his collegiate chemistry, when he is too much engrossed with what seems, to him, to be weightier matters. The Chemical Engineering Education Conference "regards English as one of its most effective tools," and recommends "a special course in report writing and the oral presentation of projects." The haste to cover ground in a limited space of laboratory time has often resulted in abbreviating laboratory records, until they are simply answers to questions. The record of high school chemical experiments should contain clear cut, accurate statements of the purpose, operation, observations, based on the operation, and conclusions drawn from the observations. The conclusion should be the goal of the purpose, and between these the logical steps of operation and observation should be stated. All should be written in the student's own language, except the purpose. The repetition of this at the experiment table as soon as the experiment is performed will fix habit. It is just as important to know the conditions under which observations were made as it is to know the observations. Writing them both serves to unite and fix this important combination in the student's mind, as well as to acquaint him with a method of making records that will be of service in the further study of chemistry.

Plainly, if the high school students in chemistry are to possess in a marked degree the ability to observe, have a clear working knowledge of certain fundamental principles, and can make good clear complete



records of experimental work, then the high school teacher of chemistry must not be a high pressure speed artist, driving on the highways to college chemistry, for the desire to cover too much ground is dangerous. The high school is distinctively a place for the development of those three things, with the paramount virtue of thoroughness. Again, too much speed in high school chemistry is detrimental to the all-important matters of relationships and generalisations. Isolated facts must be co-ordinated into a system, if they are to have power. It is not enough to know, for example, that sodium chloride and sodium nitrate will produce, respectively, hydrogen chloride and hydrogen nitrate, but that, in general, all chlorides and all nitrates behave in a similar manner; or that carbon not only reduces copper oxide, but acts on many other oxides in the same way.

How might any view be correlated with college chemistry and college chemistry with the high school view? Just as the Society for the Promotion of Engineering Education, and the National Engineering Societies and the National Committee on Mathematics, appointed committees which have recently made reports on the improvement of education in their respective branches, so I would suggest that the proper officers of the American Chemical Society appoint a nucleus committee, and this committee enlarge its number to include a sufficient representation. This committee should be a clearing house of the best information obtainable, and make a comprehensive study of how to improve education, covered by high schools, and articulate it with collegiate chemistry and make a report of the same to the American Chemical Society for its approval. Such a report would strengthen the central science of chemistry, which plays an important role in our individual, national, and international prosperity.

#### GENERAL NOTES.

##### HISTORY OF THE SPECTACLE TRADE.

At a meeting of the Optical Society, held at the Imperial College of Science and Technology, South Kensington, on Tuesday, November 27, 1923, Dr. M. von Rohr, of Jena, delivered the 1923 Thomas Young Oration. The date was the 123rd anniversary

of the delivery by Thomas Young of his famous Bakerian Lecture, "On the Mechanism of the Eye." The subject of the oration was "Contributions to the history of the spectacle trade from the earliest times to Thomas Young's appearance."

The lecturer divided the subject chronologically into six parts, and detailed the work done by different nations. The first period, beginning in the 13th century, extends to the invention of printing, about 1448. Comparatively few spectacles were then in use, and our knowledge of their production, distribution and price is very limited. The second period, relating principally to the growth of the South German spectacle factories from about 1450 up to 1620, is much better known. Thanks mainly to an oculist (Dr. v. Pflugk, of Dresden), our knowledge of the statutes and trade customs is quite remarkable, and exact details as regards the outward appearance of the spectacles then in use, their construction, distribution, and prices are available. At about the same time Venice must have been another important centre of spectacle manufacture, but unfortunately our knowledge of the glasses produced there is deplorably deficient. We are aware that in the early days of the telescope (the Dutch form and the terrestrial telescope, both made of single, unachromatised lenses) Venetian craftsmen were supplying these instruments; but of Venetian spectacles proper only some casual hints are ascertainable. In both these centres, however, "near" spectacles (for reading and working) only were made. Notable developments took place in Spain from about 1560 up to 1710: distance-spectacles fastened to the head were worn everywhere, even in the highest circles of Spanish aristocracy. This we know, not only from certain French histories that are not free from satire and irony, but also from such incontestable relics as pictures, engravings, medals. There we find high Spanish dignitaries, including a Viceroy of Naples, represented with nose-spectacles. At this time also Spanish spectacles, which were held in position by threads over the ears, were introduced to China and Japan by Spanish Jesuits. Another chapter, devoted to the decline of the South German spectacle factories between 1620 and 1780 shows the development of the cheapest nose spectacles. The chief development in this direction occurred in Nürnberg, between about 1640 and 1740, in a clever and defective manner;

it is only a pity that the makers' principal object was to turn out the greatest quantity of extremely cheap (and sufficiently nasty) goods. The last part of the lecture described the growth of the spectacle grinding optician, and related principally to the London opticians of the 18th century. The patent specifications have preserved exact data with regard to the aims and methods of these old craftsmen. The greater accuracy indispensable with achromatic objectives (invented by Chester Moor Hall in 1733 and put on the market by John Dolland after 1758) placed the London spectacle maker proper on a much better footing than his Nürnberg competitor working with bad tools and to a very small degree of accuracy.

#### THE PREPARATION OF PURE SILVER STIBIDE.

BY EDWARD J. WEEKS, M.Sc., F.C.S., AND WILLIAM V. LLOYD, B.Sc., F.C.S.

In a previous communication (*The Chemical News*, 1923, CXXVII., 319), one of us (E.J.W.) showed that silver stibide could be prepared by passing stibine into dilute silver nitrate in the cold. It has now been found possible to prepare this compound in the pure state in the following way.

Stibine is prepared electrolytically by reduction of a pure antimony cathode in N. sulphuric acid (Sand, Weeks and Worrell, *J.C.S.*, 1923, CXXIII., 456-470), and after being washed and dried it is passed through some half normal silver nitrate in the cold. Silver stibide is then deposited in the pure state. The silver was estimated in the following way:

The silver stibide was boiled with concentrated nitric acid for about half an hour and then concentrated hydrochloric acid was added and the whole further boiled for half an hour. The antimony went into solution and the silver was deposited as silver chloride. The solution was diluted, and the chloride estimated in the Gooch. The theoretical percentage of silver is 72.92 per cent., and the estimated amount was found to be 73.01 per cent.

The fact that the nitric acid produced by the action of the stibine on the silver nitrate does not oxidise the silver stibide as shown by H. Reckleben (*Ber.*, 1909, XLII., 1458-1464) is no doubt accounted for by the fact that in this method of preparation the whole action is conducted in an atmosphere of hydrogen produced from the antimony cathode.

Sir John Cass Institute, Aldgate.  
November 10, 1923.

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL SOCIETY OF ARTS.

On Monday, December 3, Cantor Lecture (1), entitled *Recent Progress in the Wool Industries*, was read by ALDRED F. BARKER, M.Sc., Professor of Textile Industries, the University, Leeds.

On Wednesday, December 5, at the Ordinary Meeting, a paper entitled *The Work of the Royal Botanic Gardens, Kew*, was read by ARTHUR WILLIAM HILL, M.A., Sc.D., F.R.S., F.L.S., Director of the Royal Botanic Gardens, Kew. Prof. C. A. Seward, M.A., F.R.S., F.G.S., F.L.S., presided.

On Friday, December 7, at a meeting of the Indian Section, a paper entitled *The Archives of the Honourable East India Company*, will be read by WILLIAM FOSTER, C.I.E., Historiographer, India Office. (Sir eGorge Birdwood Memorial Lecture.) The Right Hon. Viscount Peel, G.B.E., Secretary of State for India, will preside.

##### THE FARADAY SOCIETY.

GENERAL DISCUSSION ON "ELECTRODE REACTIONS AND EQUILIBRIA," NOVEMBER 26.

*The Mechanism of the Reversible Electrode*, by ERIC H. RIDEAL.

One of the oldest unsolved problems in physical chemistry is the source of E.M.F. in the simple galvanic cell and the mechanism of its production. Ever since the investigations of Volta, opinion has swung to extremes, oscillating between the contact and the chemical theories. At the present time there are supporters of each view, whilst a centre party of opinion wishes to ascribe the observed potential differences to both effects.

For our purpose we must exclude all irreversible effects caused by film formation at the electrodes or alteration in concentration of the electrolytes at the electrode surfaces due to a difference in the rate of removal of the ions from the skin in contact with the electrode and the rate of supply by diffusion.

A close examination of the literature on the capillary electrometer may readily lead

to the conclusion that the problem of the factors influencing the surface tension of a curved mercury surface in contact with an electrolyte have not yet been solved. It is possible that the Quincke double layer has no objective existence, and that the interfacial electrification is the result of ionic adsorption. The data of Smith and others clearly point to both cationic and anionic adsorption, whilst the Lipmann curve may be as readily deduced from the Gibbs surface tension equation as from the hypothesis of a Quincke electric double layer.

*Oxidation and Reduction Potentials of Organic Compounds*, by EINAR BULMANN.

The affinity of organic chemical processes has only been measured in very few cases of distinct transformations. Since 1920 several investigations on affinity giving numerical values have been carried out on reduction-oxidation potentials, especially of the type quinone-hydroquinone. I have tried to study the reduction potentials of some few quinones in electrolytes with different hydron concentration.

The quinhydrone, the quinone-quinhydrone, and the hydroquinone-quinhydrone electrodes were described, and an account was given of the reduction potentials of different quinones and of azo-compounds.

*The Processes at the Mercury Dropping Cathode. Part I.—The Deposition of Metals*, by JAROSLAV HEYROVSKY, D.Sc., Ph.D., Charles' University, Prague.

Experimental results have shown that a polarised drop of a mercury capillary cathode represents a reversible state of equilibrium. On each polarised drop instantly the number of ions is deposited sufficient to charge it by their solution tension to the balancing back E.M.F. The almost streamless condition of polarisation excludes the secondary effects of the current so far that the potentials at which ions are deposited from various concentrations change like the potentials of concentration cells with reversible metallic electrodes. Thus this arrangement allows an extension to the study of tri- or tetra-valent ionic concentration cells. Further, since the freshly deposited atoms are always in an active condition; the conclusion seems justified, that any retardation phenomena observed in the deposition cannot be due to surface conditions, but must be rather sought in an imperfect ionic equilibrium of the solution (*e.g.*, in the case of arsenic).

This circumstance enables us also to decide whether some metallic compounds exist as a true or as a colloidal solution.

The applicability of this method is limited on one side by the most un noble lithium deposition-potential at about  $-2.1$  volts from the normal calomel electrode, on the other it stretches to  $+0.2$  volt, where the oxidation of mercury begins.

Finally it may be pointed out that the method can be equally adapted for the study of monaqueous solutions (see Dr. Shikata's subsequent communication).

*The Processes at the Mercury Dropping Cathode. Part II.—The Hydrogen Overpotential*, by JAROSLAV HEYROVSKY, D.Sc., Ph.D., Charles' University, Prague.

The chief circumstance that allows us to follow the metallic deposition at the dropping mercury cathode up to cathodic polarisations over  $-2.0$  volts (from the calomel electrode potential) is the high overpotential displayed at the dropping mercury.

The real value of the overpotential of hydrogen, *i.e.*, the potential at which bubble formation takes place referred to the hydrogen electrode in the same solution, is thus in normal hydrochloric acid above  $-0.9$  volt ( $-1.2$  from the calomel electrode); the overpotential in more dilute acids is still greater.

It seems as if the presence of hydrogen ions catalyses the production of hydrogen; probably because the more acidic solution exerts a stronger oxidising influence upon the diffusing gas, which is then more readily removed from the electrode.

However, before the increase due to the deposition of hydrogen is reached (below  $-1.0$  volt) the dropping electrode behaves in the presence of hydrogen ions exactly as in neutral or alkaline solutions, indicating a similar state of polarisation equilibrium in the drop surface.

The experience with polarisation phenomena at the dropping mercury cathode leads necessarily to the view that only hydrogen atoms are electrochemically active at an overcharged electrode, its potential depending on the relatively very few hydrogen atoms present at the cathode; after the union to molecules the gas, which is far from being in equilibrium with the atoms, is electrochemically inactive and escapes.

The abnormally high overpotential at the dropping cathode is certainly largely due to the clean freshly formed mercury surface; however, the chief factor of the overpoten-

tial must not be sought in the ideal smoothness of the surface—as is sometimes believed—but rather in the cathode material itself.

The author suggests that ions of un noble atoms, when depositing at the charged electrode below their deposition potential, pass instantly again into solution; the number of depositions is slightly greater than the number of atoms, which leave the surface, so that each atom stays only a very short instance at the surface. If now an electrode material, like mercury, has no affinity for hydrogen nor exerts any physical adhesion to keep the hydrogen atoms longer at its surface or absorbs them inside the metallic phase, the atoms of hydrogen stay too short a time to have sufficient chance to come closer together and to combine; only at very negative potentials, when their deposition is more dense, union to molecules can proceed. The molecules then freely diffuse off or collect into bubbles. If, however, the electrode is capable of absorbing to some extent the deposited atoms, and thus shields them against the dissolving action of the solution, the atoms have occasion to combine below the surface, and escaping as molecules affect in such cases the polish of the electrode.

Some influence of a real chemical hydride formation could explain disturbances sometimes encountered at the dropping cathode during electrolysis of calcium and lithium salts, which were due to occasional bubble formation at the mercury drop. The hydrogen here evolved might be due to the union of the deposited atoms  $\text{Li} + \text{H}$  or  $\text{Ca} + 2\text{H}$  to hydrides, which are well known to be highly unstable in water and would in the aqueous layer at once form molecular hydrogen.

*Note on the Standardisation of the Sign of the Potential*, by PROF. A. W. PORTER, F.R.S.

*Determination of the Affinity Constants of Bases by the Hydrogen and Quinhydrone Electrodes*, by J. N. PRING, M.B.E., D.Sc.

A determination has been made of the hydrolysis and affinity constants of a number of amino bases in water and in acetone-water mixtures.

Both hydrolysis and affinity constants are affected by the nature of the solvent to an extent which it has not yet been possible to

correlate with any other property such as dielectric constant.

With a few exceptions, bases which are arranged in order of decreasing basicity in water have the same order as a similar series in the other solvents employed.

A determination of the dissociation constant of water has been made in acetone-water mixtures. As in the case of the affinity constants of bases, the value of the dissociation of water falls rapidly with increasing acetone content.

The author expressed his indebtedness to Mr. G. M. Westrip and Mr. T. K. Brownson for their collaboration in this investigation.

*Electrode Potentials in Non-Aqueous Solutions*, by EMIL BAUR.

Only one single method is available for the determination of a single potential difference between an electrolyte and a metallic-conducting electrode. The method is based upon an evaluation of the electrocapillary curve of mercury. Investigating this curve, G. Lippmann showed that the surface tension of mercury passes through a maximum when the polarisation is gradually being raised. At this maximum the charge on the mercury, and hence potential of the mercury against the liquid with which it is in contact, must be zero. From this consideration Helmholtz and W. Ostwald concluded that the measurement of the potential required for attaining the maximum of the Lippmann curve, would determine the potential which is effective at the mercury electrode under examination in its polarisation. When, and in so far as, this potential is identical with the voltaic potential, *i.e.*, the change in free energy, under the conditions prevailing, of the transition of mercury into mercurous ion, it must be permissible to determine the voltaic potential with the aid of the maximum of the Lippmann curve.

It has subsequently become clear that the assumption of this equality is not always justifiable. When so-called capillary-active ions are being adsorbed at the phase-boundary, the double layer of ionic adsorption will be superposed upon the Nernst-Helmholtz double layer.

Recent measurements allow us to conclude that in the case of inorganic salts the interface potentials corresponding to the partition equilibrium will generally be of little significance, amounting, perhaps, to 1

centivolt. Consequently we can fix absolute values for the electrode potentials in any non-aqueous solutions.

*Concentration Cells and Electrolysis of Sodium Ethoxide Solutions*, by DR. MASUZO SHIKATA, Imperial University of Kyoto.

To investigate the mercury dropping electrode for the study of electrolysis in non-aqueous solutions, this method has been tested on sodium ethoxide solutions. The reason for selecting the ethoxide solutions was not only their simplicity of composition and preparation, but the lack of information on this subject.

The chief aim concerning the dropping mercury method was to show that the deposition of sodium into the mercury drops from ethoxide solutions proceeds reversibly. This can be proved by comparing the shifts of the current-voltage curves with the potentials of ordinary concentration cells with sodium amalgam electrodes.

According to Heyrovsky, the sudden increase of current observable from a certain potential of the polarised drop is due to the formation of a very dilute amalgam of a certain composition, which begins to diffuse into the interior of the drops. This amalgam then must have the same composition, whether coming from any aqueous or non-aqueous electrolysis.

Therefore, if we could refer the "deposition potentials" of the polarised drops in alcohol or water to the same sodium amalgam electrode, we should obtain in either case an identical potential difference.

The deposition of sodium from alcoholic ethoxide solutions at the dropping mercury cathode was found to proceed reversibly as in aqueous solutions.

The activities of sodium ions measured by concentration cells with sodium amalgam electrodes showed an abnormal increase in concentrated solutions.

Conductivities and vapour pressures of these solutions suggest this anomaly to be due to the diminution of solvation of sodium ions.

(To be continued.)

#### THE CHEMICAL SOCIETY.

ORDINARY SCIENTIFIC MEETING, THURSDAY,  
DECEMBER 6.

The following papers were read:—

*The Additive Formation of Four-Membered Rings*. Part III. *A System of Nomenclature for Heterocyclic Four-Membered*

*Rings and the Formation and Properties of some Derivatives of  $\beta$ -Methylenedi-Imine-oxide*, by C. K. INGOLD.

*The Dependence of Polarisation-over-voltage on Hydroxyl and Hydrogen Ion Concentration*. Part I. *Polarisation-over-voltage of an Antimony Cathode in Aqueous Alkaline Solution*, by H. J. S. SAND and E. J. WEEKS.

*Stereoisomerism and Local Anæsthetic Action in the  $\beta$ -Eucaine Group*. *Resolution of  $\beta$ - and Iso- $\beta$ -Eucaine*, by H. KING.

*$\beta$ -Alizarin*. *An Isomeric Form of Alizarin*, by A. GREEN.

*The Isomerism of the Oximes*. Part XV. *The Supposed Fourth Benzildioxime*, by O. L. BRADY and F. P. DUNN.

*The Alternation in the Heats of Crystallisation of the Normal Monobasic Fatty Acids*, by W. E. GARNER and F. C. RANDALL.

#### ROYAL INSTITUTION OF GREAT BRITAIN.

A general monthly meeting was held on December 3.

#### THE INSTITUTION OF ELECTRICAL ENGINEERS.

*The Relations between Damping and Speed in Wireless Reception*, by L. B. TURNER, M.A.

The first part was devoted to an examination of the ordinary method of recorder working in wireless telegraph receivers, as affected by the damping of the receiver circuits. After a résumé of the significances of the decrement of any oscillatory system, its bearing on the possible speed of recording Morse signals is investigated. The quality (approach to correct Morse "shaping") is estimated from calculated curves of amplitude of oscillation set up in the receiver by the incoming dots and dashes constituting the letter "I." By comparing several such curves, a minimum practical value is found for the product of frequency and decrement and duration of Morse dot. The relation between speed of signalling and the requisite transmitter power is then investigated. Part I. concludes (Section 5) with a summary and discussion of the results arrived at.

An improved method of reception, called

"receiver curbing," was described and analysed. An estimate is made of the improvement obtainable, and practical circuits are given for putting the method into effect.

#### NOTICES OF BOOKS.

*Systematic Organic Chemistry*, by WILLIAM M. CUMMING, B.Sc., F.I.C., I. VANCE HOPPER, B.Sc., A.R.C.Sc.I., F.I.C., and T. SHERLOCK WHEELER, B.Sc., A.R.C.Sc.I., A.I.C. Pp. XXII. + 535. 1923. London: Constable & Co., 10-12, Orange Street, W.C.2. 25s. net.

Organic Chemistry has become so complex, abounding in complicated formulæ, and including long series of preparations and catalogues of constants and properties, that the task of writing a systematic practical volume, such as this, is very great.

The three authors have endeavoured to produce a complete laboratory guide for the up-to-date methods of preparation and estimation of organic compounds. The introductory chapters deal with general hints and practical information. The compounds are then studied in groups, and according to the linkings of the carbon atoms, *e.g.*, carbon to carbon, hydrogen to carbon, oxygen to carbon, etc. Aliphatic and aromatic bodies are discussed together in their systematic groups. Altogether, in this section, 178 reactions are studied, involving the description of 381 preparations. This is not all, however, since, in the chapters on dyes, drugs, electrolytic and miscellaneous preparations the number is brought up to nearly 500.

Many methods given in recent researches have been included.

There are nine chapters dealing with the various processes of qualitatively estimating different elements and radicals in various types of compounds; many of them are of very considerable technical and industrial importance. The last two chapters are concerned with the reagents and with qualitative tests.

Great care has evidently been taken in arranging the matter, which is very ably presented, and it would be out of place to make more than reference to the small omissions (*e.g.*, the alternative method of estimating the  $\text{NO}_2$  group), which might have been incorporated in this very comprehensive volume.

The book should commend itself to those engaged in directing advanced organic laboratory work. It is the type of book specially suited for students reading for final examinations, and for post-graduate workers.  
J.G.F.D.

*Practical Mathematical Analysis*, by HORST VON SANDEN, translated by H. LEVY, M.A., D.Sc., F.R.S.E. Pp. XV. + 195. London: Methuen & Co., 36, Essex Street, W.C.2. 1923. Price 10s. 6d. net.

This translation on applied mathematical methods is of interest, since it bridges the gap between the theories and their practical applications. The methods are developed with the object of expressing the results in a numerical form.

In the preface, the author urges that the slide-rule should be made a subject of school study. An explanation of its principles would certainly enable the conception of a function and the relative limits of accuracy to be introduced with more ease.

The book is of interest to experimentalists in the various pure and applied sciences.

*Landolt-Börnstein, Physikalisch-Chemische Tabellen*. Funfte Umgearbeitete und vermehrte Auflage, herausgegeben von DR. W. A. ROTH und DR. K. SCHEEL. In zwei Bänden Berlin: Verlag von Julius Springer. 1923. £9 7s. 6d.

Eleven years have elapsed since the fourth edition of *Landolt-Börnstein* appeared.

During this period physics and chemistry have developed very considerably, adding data to the enormous amount already accumulated.

The new matter in the present edition includes chapters on Radioactivity, Spectrum Analysis, The Physics of the Atom, Crystal Structure, etc. Other sections have been enlarged, so that the work is a really remarkable achievement, reflecting great credit upon the authors and their collaborators.

*The Journal of Scientific Instruments*: Issued by the Institute of Physics, 10, Essex Street, Strand, London, W.C.2.

The first issue of this Journal, October, 1923, brings to our notice its purpose in describing methods for measurement and the

construction of instruments in connection with all branches of scientific work. This is the first publication of its kind in England, and we have much pleasure in heartily welcoming it as being a medium of great utility to the scientific worker.

Under the management of the Institute of Physics, and with the co-operation of the National Physical Laboratory, this monthly publication should become a medium of national value.

The Editorial Board is a strong one, including Sir R. T. Glazebrook, K.C.B., F.R.S., Sir J. J. Thomson, O.M., F.R.S., and others of eminence. The secretary, F. S. Spiers, O.B.E., B.Sc., may be communicated with in regard to all matters other than those customarily dealt with by the editor, such as MSS.

#### BOOKS RECEIVED.

*Uses of Waste Materials*, by Prof. ARDURO BRUTTINI. Pp. XX. + 367. 1923. Messrs. P. S. King & Son, Ltd., Orchard House, 2 & 4, Great Smith St., Westminster. 12s. net.

*Lead*, by J. A. SMYTHE, Ph.D., D.Sc. Pp. VI. + 343. 1923. Messrs. Longmans, Green & Co., 39, Paternoster Row, E.C.4. 16s. net.

#### PUBLICATIONS RECEIVED.

The Royal Technical College, Glasgow, has just issued the Annual Report on the One Hundred and Twenty-seventh Session. It contains an account of the Studies pursued and the successes obtained, and also the general information to be found in College Calendars.

The publications and papers on research work carried out by investigators at the College indicate that there is great activity in the Chemical Department.

*Report 1921-22*, with the Supplement to the "Guide to the Experimental Plots," containing the yields per acre, etc., has just been issued by the Rothamsted Experimental Station, Harpenden, and may be obtained from the Secretary, price 2s. 6d.

The work done during the period under review is given, and there is a summary of the results of original investigations which have been published in various journals.

The report is a further striking indication of what can be achieved by the constant and

continued application of science and scientific principles to crop production and cultivation.

The Department of Overseas Trade has issued, through H.M. Stationery Office, a *Report on the Economic Situation of the Netherlands East Indies*, to June, 1923, by H. A. N. BLUETT, British Commercial Agent for the Netherlands East Indies, Batavia. 1923. Price 3s. net.

The report contains a general review of the trade of the Netherlands East Indies for the period, and indicates the prospects for the near future.

The fact that the Netherlands East Indies is a considerable consumer of chemicals and chemical manures is now fully realised by British manufacturers, and exports to this country from the United Kingdom have been well maintained.

For several of the principal lines consumed there is an increased import which has largely favoured Great Britain. Many home manufacturers previously not represented in this market have during the past two years established trade relations with leading importing firms, so that if our competitive prices are maintained there is now every indication that in future the United Kingdom will be the principal supplier of heavy chemicals.

In addition to heavy chemicals there is a good demand for refined chemicals, medicines, patent medicinal foods and photographic chemicals, also chemicals required for the manufacture of aerated waters, syrups and cordials.

*Artificial Dyes and Paints*.—The import of dyes, which are much needed for the batik industry, remains steady, although with the exception of synthetic indigo the imports for 1922 show a decrease on 1921. It should be noted, however, that stocks at the end of December, 1922, were much lower than at the beginning of that year, and as the present demand for the batik industry is good, it is expected that imports for the current year will show an increase on 1922.

*Livingstone College Annual Report*, 1922-23.

*Chains for General Engineering Purposes*. Price List. Hans Reynold, Ltd.

BULLETINS ISSUED BY THE  
DEPARTMENT OF THE INTERIOR,  
UNITED STATES GEOLOGICAL  
SURVEY.

*Gold, Silver, Copper, Lead and Zinc in the Eastern States in 1922*, by J. P. DUNLOP. Pp. 77 + 14.

*Bauxite and Aluminum in 1922*, by JAMES M. HILL. Pp. 87 + 96.

*Antimony in 1922*, by EDWARD SAMPSON. Pp. 107 to 112.

*Fluorspar and Cryolite in 1922*, by HUBERT W. DAVIS. Pp. 15 to 22.

*Salt, Bromine, and Calcium Chloride in 1922*, by K. W. COTTRELL. Pp. 23 to 29.

*Asbestos in 1922*, by EDWARD SAMPSON. Pp. 31 to 37.

*Nitrates in 1922*, by GEORGE ROGERS MANSFIELD. Pp. 39 to 40.

*Graphite in 1922*, by ARTHUR H. REDFIELD. Pp. 63 to 68.

*Boundaries, Areas, Geographic Centres and Altitudes of the United States and the Several States* (with a brief record of important changes in their territory), by EDWARD M. DOUGLAS. Pp. VI. + 234.

*Triangulation and Primary Traverse, 1916-1918*, by C. H. BIRDSEYE. Pp. 914.

*Rock Formations in the Colorado Plateau of South-eastern Utah and Northern Arizona*, by C. R. LONGWELL, H. D. MISER, R. C. MOORE, KIRK BRYAN, and SIDNEY PAIGE. Pp. 23.



THIS list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

28997—Chemische Fabrik Griesheim-Elektron.—Manufacture of acylacetyl compounds. Nov. 16.

*Specifications Published this Week.*

*p*-Nitrophenetol is prepared by heating an aqueous alcoholic solution of *p*-nitrochlorobenzene of low concentration with a quantity of an alkaline reagent, such as sodium ethoxide, not substantially in excess of that chemically equivalent to the chloro-derivative, at or above the normal boiling-point of the aqueous alcohol and without ebullition. For concentrations of the chloro-derivative of 3 per cent. and upwards, less than the equivalent of the alkali may be used. According to examples, concentrations of 3 and 5 per cent. of *p*-nitrochlorobenzene in 85 per cent. alcohol are heated with sodium ethoxide and caustic soda respectively in an autoclave and at temperatures of 90-120° C. To prevent reduction to azoxy-compounds the autoclave is lined with enamel, silver, or nickel.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

## NOTICES.

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## THE CHEMICAL NEWS,

VOL. CXXVII. No. 3322.

ARE THE NATURAL GROUPINGS OF  
THE ELEMENTS AND THE SPECTRAL  
LINES OF HYDROGEN RELATED?

## PART VI.

By F. H. LORING.

In continuation of the above study from *The Chemical News*, 1923, CXXVII., p. 355, the following observations will be given:—

## NOTES AND COMMENTS.

1.—The advent of the octet theory of atomic structure and the planetary theory of the atom as developed by Niels Bohr has placed before chemists a quantity of valuable theoretical matter which is difficult to harmonise; for, How can the electrons describe elliptical and circular orbits round atomic nuclei and at the same time function as practically stationary bodies disposed round each nucleus in various patterns as demanded by the followers of the octet theory?

It has been suggested in this paper that the Bohr orbits are in reality radiation orbits, and that the vibrations of the electrons are electro-mechanically equivalent to such orbits. It was shown that ponderable mass as such need not be a factor in the phenomena of orbital paths, since the orbits were not finally governed by the moving mass magnitudes; but, on the other hand, *velocity* is an important factor. In addition to this, the *entrant direction* of the moving entity should be taken into account. For example, a comet entering the solar system in a certain direction, i.e., moving towards the immediate region of the sun, while then travelling with a certain velocity, will fall under the sun's influence and describe a certain orbit round it. At the most distant part of its orbit, that is to say, at its aphelion, the comet is moving at a momentary zero velocity relative to the sun, and it is then that it changes its direction and returns to the region of the sun, the orbit being elliptical: just as a ball thrown upwards from the earth comes instantaneously at rest relative to the earth at a certain height, and then falls back to the earth, describing an ellipse having no area—which is a straight line. Whether the ball be light or heavy, without

air friction it could be made always to describe the same path or orbit of zero area, and its acceleration would be the same also. In this case the mass of the ball is not a factor in the time-rate-of-change of velocity.

The planets, that travel out orbits in accordance with the place law of Bode, vary irregularly in mass in respect to one another, so that no direct connection between mass and the particular orbit selected is possible. Again, the effect of mass is an antecedent one, and this is an important matter, for mass is functionally a prior condition in the phenomenon, which is related to the energy expended in producing the initial velocity, and of course the mapping of the subsequent velocities as well, for it determines the velocity at which a given body may enter a planetary system; or, in the instance of the ball, the height to which it is thrown by the thrower.

Now, if the orbits which the planets describe be regarded as definitely predetermined places in space, this "predetermination" must rest upon the antecedent factors just indicated, so that any orbit is possible, according to the entrant direction and velocity, which may be considered jointly; and this joint effect in turn rests upon the preceding event in which the energy (1) acting on the mass (2) were the predominating factors. The whole phenomenon dates back, as it were, to the initial energy and mass conditions, which have to be considered retrospectively with regard to the entrant direction and speed at a given place relative to the sun.

The orbit in the hydrogen atom must similarly depend upon the initial energy conditions if the phenomena discussed are of a parallel nature, as would seem to be the case. The formation of the planetary system then is akin to the condition of affairs that takes place in the spectrum processes of hydrogen; but, the question arises—How far back are the antecedent conditions to be carried?

Considering the atom, since there is only *one* electron belonging to hydrogen, the antecedent conditions do not in the several processes of radiation go back as they do in the planetary system, containing nine planets (counting the asteroids collectively as one). Moreover, since the hydrogen orbits are mathematically regular and always the same when they are rendered, so to speak, visible by the resulting emission lines, the energy conditions as regards direction and velocity is always the same

for each line. How, then, can this state of affairs be explained?

It seems that the electron can only take up energy in multiples of a given quantum, and give out energy in the same multiples, according as the electron is driven from one "orbital" place (radial place) to another, and this is quite in accord with Bohr's quantum-energy theory of the hydrogen atom. The electron can only take up and give out a quantum of energy which corresponds to its position relative to the nucleus, and therefore it must be under a constraining influence to do this; so that what corresponds to the antecedent event in the case of the planetary system is practically concurrent with the radiation phenomena of the atom.

This, then, involves the *energy* and *mass* of the electron, if the case is like that of the planetary system; but since the mass factor under consideration is not necessary to the orbit as such, it can be regarded as the determining factor in the *vibration* of the electron. In other words, in the case of the atom the antecedent factor is the vibration of the electron. The immediately subsequent factor is the radiation which, according to this view, describes practically closed orbits round the nucleus, and the final occurrence is the passage of this radiation out as a radial radiation when the electron is driven or falls towards the nucleus into another position of equilibrium in which it vibrates according to its place. The influence of the sun, or the atomic nucleus, is of course most important; but the observations are here concerned more particularly with the behaviour of the orbits in respect of their relative spacial positions.

2.—One difficulty that arose from the many-electron orbits of Bohr's theory was the complex magnetic phenomena which should theoretically arise from so many circulating negative electrons corresponding in effect to closed electric circuits. The hydrogen atom should then behave like such a circuit and exhibit magnetic effects; and many elements should show similar effects; whereas, only a few elements give rise to strong magnetic phenomena, these being iron, cobalt, nickel. Now, in the atoms of these three elements there may be electrons so situated that, under certain related conditions, they are free to describe orbits, but in practically all other elements the electrons can only vibrate, as according to this study such a conclusion seems inevitable.

3.—Referring to the wedge periodic table.

attention should be drawn to a feature of some suggestive value; that is to say, the characterisation of the element by the width of the wedge where the element falls. In science, geometric representation of a quantity or quality, in which the origin of the plan is not known, is often more truly scientific because of its non-committal nature; for truth is often better expressed by a non-committal scheme than by one based upon highly artificial and ingenious hypotheses.

4.—In referring to the spectral lines of hydrogen, it should be noted that there are several types of spectra, namely: (1) the Balmer series lines; (2) the many-lines spectrum, called the secondary spectrum of hydrogen; (3) the Lyman series lines; (4) the Paschen series lines; (5) the Brackett series lines; (6) a continuous spectrum without lines; (7) a fine-line series due to the relativity effect in connection with each so-called single line. In the case of the Balmer series, it is frequently expressed mathematically in  $\nu$  terms, as are also the others of like type, as follows:—

$$\nu = N \frac{1}{1^2} - \frac{1}{n^2} \quad (\text{Lyman.})$$

$$\nu = N \frac{1}{2^2} - \frac{1}{n^2} \quad (\text{Balmer.})$$

$$\nu = N \frac{1}{3^2} - \frac{1}{n^2} \quad (\text{Paschen.})$$

$$\nu = N \frac{1}{4^2} - \frac{1}{n^2} \quad (\text{Brackett.})$$

$N$  = the Rydberg constant.

The *frequency* equals the velocity of light ( $c$ ) in centimetres per second divided by wave length ( $\lambda$ ), also in centimetre measure; but the Rydberg constant is usually evaluated by the equation in which  $\nu$  = *wave number*, or  $1/\lambda$  cm., so that

$N = (4n^2/n^2 - 4) \times (1/\lambda \text{ cm.})$ , in which  $n$  for the Balmer series runs 3, 4, 5, 6, 7, &c.

5.—Referring to the planets and the group numbers, the average percentage of error, not counting the asteroids, is as follows:—  
 $(-0.29) + (-1.16) + (-0.33) = (-2.78)$ .  
 $(-2.78/3) = (-0.926)$ .  $(-0.926) - (+0.28) = (-0.646)$ .  $6.72 + 9.29 + 14.16 + 48.33 = 78.50$ .  $78.50/0.646 = 121$ .  $100/121 = 0.8$  per cent. The respective summations are 77.0 and 78.50.

6.—Referring to Bode's law, it will be seen that it is not mathematically regular in respect of the first term; and that it de-

parts appreciably from the planetary values above 52.02. Similarly, the group rule indicated agrees with the planetary values just where Bode's law agrees, thus suggesting that the complete law of the planets is perhaps expressible by two formulæ.

7.—The coronium line, 5303, would by the formula given correspond to the upper limit of the asteroids, for it would give a value 28.7. The mean  $28.7 + 21 = 24.8$ , which is close to the asteroid mean of 25. No importance whatever can be attached to this observation; but it is given to show that strange lines might be considered in connection with the relations given.

8.—Having accorded preference to Vegard's theory in respect of the constituent of the upper atmosphere, attention may be here drawn to another theory, equally valuable for the purpose of the main argument, due to H. Bongards (*Phys. Zeit.*, 1923, Vol. XXIV., p. 279). This paper is abstracted in *Science Abstracts* for November, 1923; and to give the readers of *The Chemical News* this information, the abstract is mainly reproduced here: "Slipher found for the wave-length of a green line discovered by Wiechert in the night sky of middle latitudes the wave-length 5578.05 Å, while Vegard found  $\lambda = 5578.2 \pm 1$  for what is generally regarded as the same line in the aurora. A faint line in the multiple line spectrum of hydrogen,  $\lambda = 5578.3$ , can hardly be identified with this; and the only other known line of the right wave-length is  $\lambda = 5577.98$  in the blue spectrum of argon. There are many other lines in this spectrum and in that of the aurora; but so far the latter has not been measured with sufficient accuracy to allow of identification, as the number in both cases is so large at the violet end of the spectrum; but there is additional evidence in the fact that in the red portions of the aurora Vogel found two bright lines,  $\lambda = 6297$  and  $\lambda = 5189$ ; these measurements were taken in 1871, and are regarded as fairly accurate. In the red argon spectrum, which appears to be due to argon atoms which have lost one electron, Paschen found a bright line,  $\lambda = 6297.15$ , and Kayser another,  $\lambda = 5188.46$ ; these are probably identical with the above auroral lines. In spite of its high density argon may be present normally in the atmosphere at heights above 100 km. where the aurora is seen; volcanic eruptions may carry this gas to great heights, and the thermodynamical properties of monatomic gases favour their remaining at high elevations when they

have attained them; the author, however, favours the view that argon particles are ejected from the sun, with very high velocities, and entering the earth's atmosphere produce the aurora. There are difficulties in the way of this theory. The absence of Doppler effect indicates a velocity less than  $3 \times 10^7$  cm., which would not enable the particles to penetrate so deep into the atmosphere; the argon particles may leave the sun strongly positively charged, with a very high velocity, and being devoid of the electrons which are concerned in radiation do not begin to emit light until, by collisions with the atoms of the air, they have lost much of their velocity, and picked up the necessary electrons. . . ."

#### A MODIFIED VIEW OF THE ATOM ARISING OUT OF THIS STUDY.

9.—If the extended argument of this study is in general true in its purport, then it can be said that the natural groupings of the elements are linearly related to the wave-lengths of the first five Balmer lines of hydrogen; but still further evidence is needed before the argument as a whole can reasonably be considered sound. It was suggested that, in conformity with the findings of this study, the Bohr atom was really static as regards the electron movement other than vibration and radial displacement, and that the Lewis-Langmuir theory could stand on its own merits as a consequence.

Now it is not out of order to consider an atom-model along the lines suggested. In the first place it will be conducive to clearness to state the facts and concepts upon which such a model can be constructed. These are:—

(a) Rutherford's monumental work on the nucleus theory of the atom is based on such fine experiments and consistent reasoning that it is everywhere accepted as a fact. Stated otherwise, the atom has a nuclear part which is a positive charge corresponding in magnitude exactly with the atomic number, the latter having been experimentally established by the work of Moseley, which is well known.

(b) In view of this study it is suggested that the electron can vibrate to and fro relative to the positive nucleus in *all* positions, but only in those in which the radiation closes synchronously on the electron can it be held in a fixed place.

(c) Under these circumstances, when

the electron, as the operator, is forced by the nature of events out of the fixed place, the closed radiation passes out from the atom at the velocity of light as light or radiant energy.

In general, for a series of energetic vibrations, the spacing of the lines will be wide; but for a series of minor vibrations the spacings will be close, which follows partly from (a) and (b) above.

Certain antecedent factors may govern the "energetics" of the electron. (See note 1 above.)

The position of the electron relative to the nucleus is governed by its amplitude of vibration or *vice versa*; so that for high frequencies it is able to be nearer the nucleus than for low frequency vibrations.

The high frequency vibrations are emitted in more widely spaced quanta, in accordance with Planck's equation, than the lower frequency vibrations, being no doubt governed by the probability of the occurrence owing to the nature of the mechanism. It is as if the inner position is more difficult to attain to frequently, whereas the outer positions are more vulnerable, so to speak, and consequently the phenomenon occurs oftener.

#### Corrections.

Owing to illness when the proofs arrived, the writer was unable to make all the corrections and amendments necessary. The following may therefore be noted:—

On page 275, 25th line from top, insert "of molecular or" next to the words "atomic weight." On page 290, right-hand column, 14th line from bottom, "continued" should read "concluded." On page 337, 1st column, 2nd line of text, "272" should read "273." On same page, 2nd column, 14th line from top, "contradiction" should read "contradistinction." On page 338, right-hand column, 28th line from bottom, next to the word "will" insert: "consist of doublets, while, if the number is even the spectrum." On page 339, left-hand column, 8th line from top of paragraph beginning with "The," "each" should read "such."

## INDIGOID DYESTUFFS.

### PART II.

By R. F. HUNTER, F.C.S.

(Continued from Page 359.)

We now have to study the indigo analogues, and we shall first deal with indigo

analogues derived from two similar component nuclei, following, as before, the classification of Thorpe and Ingold.

The first dye to be considered as derived from indole, apart from indigo or 2:2' bis indole indigo, which has already been dealt with, is indirubin, indigo-red, or 2:3 bis indol indigo. This was synthesised by Bayer by condensing indoxyl and isatin. This was modified by Forrer, who replaced indoxyl with indoxyllic acid and obtained an 80 per cent. yield.

Wahl and Bagard's synthesis consists of condensing oxindole with isatin chloride.

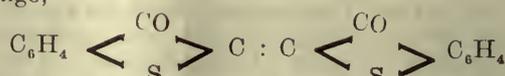
Among the substitution products mention may be made of the following:—

- 5 Methyl indirubin;
- 7 Methyl indirubin;
- 5' Methyl indirubin;
- 5':7' Dimethyl indirubin;
- 5' Bromoindirubin;
- 5':7' Dibromo indirubin;
- 5:5' Dimethyl indirubin;
- 6:6' Dibromo indirubin;
- 6:5':7' Trichloro indirubin.

The next analogue is 3:3' bis indol indigo or iso indigo, obtained by Laurent in 1841 by heating isatyde. As derivatives we have:—

- 5 Bromo isoindigo;
- 5:7 Dibromo iso indigo;
- 5 Nitro iso indigo; and as homologues:
- 5 Methyl iso indigo.

This brings us to the indigoid dyes from thionaphthen, the most important of which is thio indigo, or 2:2' bis thionaphthen indigo,



prepared in 1906 by Friedlander, by an application of the Badische modification of the Heumann synthesis, in which thio salicylic acid replaces anthranilic acid. The present synthesis consists of the conversion of phenyl thio glycollic acid into hydroxy thio naphthen, this to thio indigo white, and thence to thio indigo. Another method is to convert anthranilic acid into the diazonium salt, this to dithio salicylic acid, this to thio salicylic acid, this to *o* carboxy phenyl thio glycollic acid, thence to hydroxy thio naphthen carboxylic acid to hydroxy thio naphthen, and thence to thio indigo.

Another method is to convert aniline into *o* amino thio phenol, to *o* amino phenyl thio glycollic acid, to *o* cyano phenyl thioglycollic acid, to 3 amino thio naphthen 2 car-

boxylic acid, and this to 3 hydroxy thio naphthen. Another method depends on the condensation between thiosalicic acid and acetylene dichloride, the bis thiosalicic derivative of ethylene formed on dehydration proceeds directly to thio indigo.

Hydroxy thio naphthen can be converted into thio indigo by other means than oxidation. Thus, when hydroxy thio naphthen is brominated there are formed in no bromo and dibromo compounds, both of which readily pass into thio indigo. These methods are, of course, of no commercial value.

Thionaphthenquinone, the thio analogue of isatin, deserves mention. It can be prepared in a variety of ways. For instance, the dibromo derivative above can be directly hydrolysed, or it can be treated with aniline, the product being the anilide of thio naphthenquinone from which aniline residue is removed by acid hydrolysis.

Further, hydrothio naphthen with nitrous acid yields a nitroso compound which, on hydrolysis, yields thio naphthenquinone. Among the substitution products and homologues of thio indigo, we might mention:—

- 7:7' Dimethyl thio indigo;
- 4:6:4:6' Tetramethyl thio indigo;
- 5:7:5':7' Tetramethyl thio indigo;
- Bis 1:2 naphtha thiophen indigo;
- Bis 1:8 naphtha thiophen indigo;
- Bis 2:3 naphtha thiophen indigo;
- Bis 2:1 naphtha thiophen indigo;
- 5:5' Dichloro thio indigo;
- 5:5' Dichloro 6:6' dimethyl thio indigo;
- 7:7' Diamino thio indigo;
- 6:6' Dichloro thio indigo;
- 6:6' Diethoxy thio indigo;
- 5:6' Dibromothio indigo;
- 4:4' Dimethyl 6:6' dibromo thio indigo;
- 6:6' Dimethyl thio indigo;
- 5:5' Dichloro 6:6' diethoxy thio indigo.

2:3' Bis thio naphthen indigo, or thioindirubin, is worthy of note, and has been prepared from hydroxy thio naphthen and thionaphthenquinone.

The indigoid dyes from coumarone are of interest:—

2:2' Bis coumarone indigo, unlike its sulphur and nitrogen analogues, is not of technical importance. It has been prepared by condensation of coumaranone with p nitroso dimethylaniline, followed by hydrolysis with HCl to gem dimethyl p phenylenediamine and oxindigo.

2:3' Bis coumarone indigo, or oxindirubin, has not been prepared, but methyl derivatives are known. We might mention:

- 5:5' Dimethyl oxindirubin;
- 6:6' Dimethyl oxindirubin;
- 5:6' Dimethyl oxindirubin;
- 6:5' Dimethyl oxindirubin.

Symmetrical indigoid dyes derived from other component nuclei are known. We might mention:—

- 2:2' Bis indenone indigo;
- 1:1' Bis acenaphthene indigo;
- 3:3' Dinethyl 5:5' dimethoxy 1:1' bis benzene indigo;
- 1:1 Bis phenanthrene indigo;
- 4:4' Diphenyl bis 2:2 furan indigo;
- 5:5' Diphenyl 2:2' dimethyl 3:3' bis pyrazole indigo;
- 3:3' Bis isocarbostyryl indigo.

This brings us to the indigo analogues derived from two dissimilar nuclei, of which ciba violet A, or 2 indole 2 thio naphthen indigo, is an example

The first class of these dyes are those formed by the union of any two or three component nuclei; indole, thio naphthen, and coumarone, following the classification of Thorpe and Ingold. As dyes from indole and thionaphthen, we have 2 indol 2 thio naphthen indigo, or ciba violet A, derivatives of this being 2(5 Bromoindole) 2 thio naphthen indigo 2(5:7 dibromoindole) 2 thio naphthen indigo 3 indol 2 thio naphthen indigo, or thioindigo scarlet R, from which derivatives have been obtained.

As dyes from indole and coumarone, we have 2 indol 2 coumarone indigo and 3 indole 2 coumarone indigo.

The sole dye from thionaphthen and coumarone is 2 thionaphthen 3 coumarone indigo.

The second class of dyes are formed by the union of either of the component nuclei; indole and thionaphthen, with a six membered homocyclic ring of the benzene type. We consider firstly, the dyes derived from indole by union with six membered homocyclic rings. We have:—

2 Indole benzene indigo; this indigo has not, as yet, been prepared, but derivatives of it are known. Derivatives with hydroxyl groups in the benzenoid component nucleus have been prepared by Friedlander by condensing the appropriate polyhydric phenols with isatin chloride. We might mention the dyes from resorcinol, catechol and pyrogallol. An amino derivative has been prepared by condensing isatin chloride with m hydroxy diphenylamine.

2 Indole 2 naphthalene indigo was prepared by Friedlander by condensing a naphthol with isatin chloride in benzene solu-

tion. Derivatives have been prepared from substituted  $\alpha$  naphthols. We might mention the dyes obtained from monomethyl 1:4 dihydroxy naphthalene from 1:5 dihydroxy naphthalene and 5 acetamino 1 hydroxy naphthalene. Derivatives containing substituents in the indole nucleus have been obtained by condensing substituted isatin with naphthol.

Derivatives have been made by using azo dyes from diazotised base by coupling with  $\alpha$  naphthol in conjunction with isatin  $\alpha$  anilide.

2 Indole 1 naphthalene indigo has been prepared by Friedlander from isatin chloride and naphthol.

2 Indole 2 anthracene indigo has been prepared by the same author from isatin  $\alpha$  anilide and  $\alpha$  anthrol. Derivatives are known.

Hydroxyl derivatives have been prepared by condensation of 1:5 and 1:8 dihydroxy anthracene with isatin  $\alpha$  anilide. Some important dyes have been prepared by condensing 5 chloro, 5 bromo, 5:7 dichloro, 5:7 dibromo isatins with anthrol and 1:5 and 1:8 dihydroxy anthracene. Similar compounds have been prepared by condensing 7 methyl isatin chloride, 5:7 dimethyl isatin chloride, and 5:6 methylene dioxy isatin chloride with  $\alpha$  anthrol and 1:5 and 1:8 dihydroxy anthracene. Blue dyes have been prepared by condensing hydroxy anthrone with isatin chloride and 5:7 dibromo isatin chloride.

2 Indole 1 anthracene indigo has been prepared by Bezdrík from  $\beta$  anthrol, just as 2 indole 2 anthracene indigo is prepared from  $\alpha$  anthrol.

2 Indole 3 acenaphthene indigo has been obtained from isatin  $\alpha$  anilide and 4 hydroxy acenaphthene, by replacing 5:7 dibromo isatin chloride in place of the anilide 2 (5:7 dibromoindole) 3 acenaphthene indigo is obtained.

As dyes derived from thio naphthen by union with six membered homocyclic rings, we have:—

2 Thionaphthen 2 naphthalene indigo from  $\alpha$  anilide of thio naphthen quinone and  $\alpha$  naphthol;

2 Thionaphthen 2 anthracene indigo from  $\alpha$  anthrol and  $\alpha$  anilide of thio naphthen quinone;

2 Thionaphthen 2 naphthapheno carbazole indigo and 2 thio naphthen 2 naphthapheno carbazole indigo.

This brings us to the third class of dyes, those formed by the union of either of the

component nuclei, indole and thionaphthen, with a five membered homocyclic ring of the type contained in indene. We consider first the dyes from indole and 5 carbon rings. An example of these is 2 indole 2 indene indigo, prepared by Friedlander, by condensing isatin chloride with  $\alpha$  hydrindone.

2 Indole 1 indene indigo has been prepared from hydrindone and isatin  $\alpha$  anilide in the presence of pyridine.

2 Indole 1 acenaphthylene indigo has been prepared from indoxyl and acenaphthenquinone, and also by condensation of acenaphthone and isatin chloride.

Halogen derivatives have been prepared by using dibromo diacetyl indoxyl in the place of indoxyl or dibromo isatin in place of isatin and by direct halogenation of the parent dye.

The dyes from thionaphthen and five carbon rings are of interest.

2 Thionaphthen 1 indene indigo has been prepared by treating hydrindone with acetic anhydride and with the condensation product of *p* nitrosodimethylaniline and 3 hydroxy thionaphthen. 2 thionaphthen 2 acenaphthylene indigo, better known as ciba scarlet, has been prepared by condensing 3 hydroxy thionaphthen with acenaphthaquinone in an acetic acid solution in the presence of hydrochloric acid in small quantity as condensing agent. It has also been prepared by heating acenaphthaquinone with 3 hydroxy thio naphthen 3 carboxylic acid. Halogen derivatives of ciba scarlet are known.

2 Thionaphthen 1 aceanthrylene indigo has been prepared from 3 hydroxy thionaphthen and aceanthraquinone.

The fourth class of dyes are those formed by union of the component nucleus indole with six membered heterocyclic rings, of which 2 indole 3 isocarbostryl indigo is an example.

We conclude with the fifth class of dyes, those formed by union of either of the component nuclei, indole and thionaphthen, with five membered heterocyclic rings. 2 indole dihydroxy pyrimidine indigo is an example of a dye containing a simple six membered heterocyclic ring as one of its compound nuclei, and is prepared by condensation of isatin  $\alpha$  anilide with barbituric acid in the presence of acetic anhydride.

2 Indole 4 pyrazole indigo is the parent of a class of dyes of which only two are known at present. The 3' methyl and 1' phenyl 3' methyl derivatives have been obtained by

condensation of isatin anilide with 3 methyl and 1 phenyl 3 methyl pyrazolone.

2 Indole 2 isoxazole indigo has been prepared by condensing isatin chloride with the corresponding aromatic isoxazolone.

2 Indole 5 thia zolthiole indigo has been prepared by condensing isatin anilide and rhodanic acid in the presence of acetic anhydride.

2 Thionaphthen 5 thiazol thiole indigo, the last dye we shall consider, has been obtained from the *a* anilide of thio naphthenquinone and rhodanic acid.

*The Royal College of Science,  
October, 1923.*

### GENERAL NOTES.

A report on the present position of the stocks of drugs and chemicals, etc., in Japan has been received from the Acting British Consul at Osaka, copies of which, together with lists of importers in Japan, may be obtained by British firms upon application to the Department of Overseas Trade.

### ATMOSPHERIC CORROSION.

The First Experimental Report to the Atmospheric Corrosion Committee of the British Non-Ferrous Metals Research Association will be presented and discussed at a meeting of the Faraday Society, to be held on December 17, at 8 p.m., in the rooms of the Chemical Society, Burlington House, W.1. The very comprehensive series of field tests and laboratory experiments described in the Report were carried out by Mr. W. H. J. Vernon on behalf of the Committee. Persons interested in the subject desirous of attending the discussion may obtain a ticket of admission from the Secretary of the Faraday Society, 10, Essex St., London, W.C.2.

### PROCEEDINGS AND NOTICES OF SOCIETIES.

#### THE ROYAL SOCIETY.

THURSDAY, DECEMBER 6.

Papers read:—

E. G. T. LIDDELL and SIR CHARLES SHERINGTON, PRES. R.S., *Recruitment Type of Reflexes.*

G. S. CARTER, *The Structure and Movements of the Latero-Frontal Cilia of the Gills of Mytilus.* Communicated by Prof. J. S. Gardiner, F.R.S.

Papers read in title only:—

V. B. WIGGLESWORTH and C. E. WOODROW, *The Relation between the Phosphate in Blood and Urine.* Communicated by Prof. F. G. Hopkins, F.R.S.

It has been shown that ingestion by man of doses of the acid and alkaline sodium phosphates containing  $1\frac{1}{2}$ -2 grammes of phosphorus causes a rapid 50-60 per cent. increase in the blood phosphate, which then returns very gradually to the normal level. The work of others has shown that phosphate is so rapidly excreted by the kidneys of the dog that no such increase occurs in that animal under similar conditions.

In such experiments the curve of urinary excretion of phosphate runs roughly parallel to that of the blood concentration, but the former varies much more widely than the latter, and is roughly proportional to the excess above a certain value in the blood. Moreover, the rate of excretion in the urine is independent of the amount of water excreted.

In a study of the partition of the inorganic phosphate between the plasma and corpuscles of the blood, it has been shown that under conditions in which the blood phosphate is subnormal, normal, or slightly above normal in amount, the concentrations in plasma and corpuscles are identical. When the concentration in the plasma rises far above normal the value for the corpuscles is always lower, whether the plasma value is rising or falling. This unequal partition is not to be explained by the formation of an organic "acid-soluble" phosphorus compound in the corpuscles, for the organic fraction of the acid-soluble phosphorus is not increased by the ingestion of phosphate; nor is this fraction increased by taking glucose or a mixture of glucose and phosphate, as might have been expected if one of its constituents were a hexosephosphoric ester.

J. B. S. HALDANE, V. B. WIGGLESWORTH and C. E. WOODROW, *The Effect of Reaction Changes on Human Inorganic Metabolism.* Communicated by Prof. F. G. Hopkins, F.R.S.

Over-breathing diminishes the phosphates in blood and urine, while carbon dioxide inhalation and sleep increase them.

In acidosis caused by ammonium-chloride ingestion the urinary phosphate is increased; while the phosphate of the blood, and also its organic acid-soluble phosphorus, is diminished. Ammonium-chloride acidosis leads to an increased excretion of water, sodium, and potassium, probably owing to a partial loss of electric charge by the body colloids. This is followed by a retention.

J. B. S. HALDANE, V. B. WIGGLESWORTH and C. E. WOODROW, *The Effect of Reaction Changes on Human Carbohydrate and Oxygen Metabolism*. Communicated by Prof. F. G. Hopkins, F.R.S.

The alkalosis of over-breathing or bicarbonate ingestion converts the blood sugar into a highly dextrorotatory, unoxidisable form, and also prevents glucose storage; thus causing acetonuria and lowered respiratory quotients and glucose tolerance. Ammonium-chloride acidosis interferes with the storage of glucose, but not with its oxidation. Bicarbonate ingestion raises the resting oxygen consumption; ammonium-chloride ingestion usually lowers it.

J. A. CAMPBELL, *Concerning the Influence of Atmospheric Conditions upon the Pulse Rate and "Oxygen-Debt" after Running*. Communicated by Prof. L. Hill, F.R.S.

The "oxygen-debt" for 25 minutes after ceasing to run showed, under fixed conditions of experiment, a range of variation of 38 per cent. from day to day; 7-minute debts showed a range of 33 per cent., so should do as well for comparative purposes as 25-minute debts. Atmospheric cooling power had no effect on the "oxygen-debt"; the blood sent in greater volume through the skin in warm conditions is not then taken from the muscles. "Stitch" was the commonest cause of cessation of running in the subjects—not first-class athletes—under observation. Pulse rate is markedly increased under warm conditions. This is not always shown clearly in short experiments in cool conditions, because it takes time for the body mass to become heated up. The oxygen tension surrounding the muscles was increased after exercise.

J. GRAY, *The Mechanism of Ciliary Movement*. IV.—*The Relation of Ciliary Activity to Oxygen Consumption*. Communicated by Prof. J. S. Gardiner, F.R.S.

In the absence of atmospheric oxygen ciliary activity continues for about one

hour. From a study of the effect of various reagents upon the mechanical activity and on the oxygen consumption of ciliated cells, it is concluded that the whole ciliary mechanism is divisible into three distinct parts: (i) a reaction which is sensitive to cations (particularly the hydrogen-ion), any interference with which involves a change in the rate of the ciliary beat, but only ultimately leads to a change in the amount of oxygen consumed; (ii) a mechanism which appears to be brought into operation by the presence of an activating acid substance. This mechanism is inoperative in the absence of calcium, and in the absence of a certain critical amount of water in the cell. The events associated with this mechanism are independent of and have no influence upon the amount of oxygen absorbed; (iii) a reaction of an oxidative nature which is necessary for prolonged activity.

As far as they are at present known, the properties of the ciliary mechanism form a very close parallel to those of cardiac muscle, as illustrated by the sinus region of the heart.

#### THE INSTITUTION OF ELECTRICAL ENGINEERS.

An Ordinary Meeting was held on Thursday, December 13. A paper entitled *Pulverised Fuel and Efficient Steam Generation*, was read by D. BROWNIE.

*Pulverised Fuel and Efficient Steam Generation—A Detailed Consideration of the Performance of Pulverised Fuel as compared with Mechanical Stoking under the most Modern Conditions*, by DAVID BROWNIE, B.Sc.

The paper is a detailed consideration of the latest developments in the use of pulverised coal for steam generation, and a comparison of the advantages and disadvantages of this method of firing as compared with mechanical stoking, in each case under the latest improved conditions and more particularly as applied to very large power station boiler plants. Since the starting up in December, 1920, of the pioneer large installation, Lakeside, Milwaukee (40,000 k.w. on "Lopulco" pulverised fuel), the progress made in the United States has been remarkable, and 3,500,000 tons of pulverised coal will shortly be burnt per annum under water-tube boilers.

The paper contained a full account of the



Lakeside station, particularly the exact working costs, whilst a description was also given of the River Rouge plant at Dearborn, Detroit, as representatives of the latest pulverised-fuel practice. For comparison, a similar account is given of the Dalmar-nock power station, Glasgow, characteristic of the best British mechanical stoker practice.

The author is of the opinion that the advantages in the aggregate of pulverised fuel are so remarkable that they constitute almost a revolution in steam boiler practice. The paper also contained a large amount of general statistical matter.

A Wireless Section Meeting was held on Wednesday, December 5. A paper entitled *The Relation between Damping and Speed in Wireless Reception* was read by L. B. TURNER, M.A. (Member).

#### THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The Seventy-Fourth General Meeting was held on Tuesday, December 11, when the following paper was read:—

*The Modern Rotary Drilling System*, by L. R. McCOLLUM.

The chair was taken by the President, H. Barringer, M.Inst.C.E., M.I.Mech.E., M.I.N.A., M.Inst.Mar.Eng.

#### PROCEEDINGS OF THE GEOLOGICAL SOCIETY OF LONDON.

NOVEMBER 21.

Prof. A. C. Seward, Sc.D., F.R.S., President, in the chair.

The following communication was read and discussed:—

*The Development of the Severn Valley in the Neighbourhood of Iron-Bridge and Bridgnorth*, by LEONARD JOHNSTON WILLS, M.A., Ph.D., F.G.S.; with a Section on the Upper Worfe Valley, in collaboration with Ernest Edward Leslie Dixon, B.Sc., F.G.S.

A meeting of the Society was held on Wednesday, December 5, when the following communications were read:—

*The Geology of Southern Guernsey*, by D. J. FARQUHARSON, M.Sc. Communicated by Prof. O. T. Jones, D.Sc., M.A., F.G.S.

*The Geology of the Northern Border of Dartmoor between Whiddon Down and Butterdon Down*, by C. W. OSMAN, M.Inst.C.E., F.G.S.

Specimens and lantern-slides of Arachnid remains from the Rhynie Chert were exhibited by Dr. F. A. Bather, M.A., F.R.S., on behalf of Mr. A. S. Hirst, F.Z.S.

#### THE SOCIETY OF GLASS TECHNOLOGY.

A meeting was held in Leeds on November 21, the President, Prof. W. E. S. Turner, D.Sc., in the chair. Three papers were presented.

*Notes on the Influence of Rapid Chilling on the Reversible Expansion of Clay*, by H. S. HOULDSWORTH, M.Sc.

The author gave results of measuring the reversible thermal expansion of fireclay test pieces cooled slowly and rapidly. Test pieces were moulded from Farnley fireclay, dried and fired in the surface combustion laboratory furnace to Cone 9 (1280° C.) in three hours and maintained at that temperature for two hours more. One piece was removed from the furnace and plunged into cold water, and another was placed on a steel plate to air cool, while a third was slowly cooled in the furnace. A glass pot mixture of clay and grog obtained from Stourbridge in a leathery condition was next examined. There was a considerably greater difference in the temperature-expansion curves of the rapidly chilled and slowly cooled specimens after firing at Cone 9 than was found for Farnley fireclay. The expansion of the air-cooled test pieces was intermediate between those of the water-cooled and slowly-cooled samples. At Cone 14 (1410°) the thermal expansion of the air-cooled and water-cooled specimens were nearly the same and considerably less than that of the slowly cooled test pieces.

The whole of the phenomena were consistent with the explanation that solution of free silica occurred at higher temperatures, and separated out as cristobalite or tridymite on slow cooling, exerting its characteristic influence on the expansion curve, but that it did not so separate on rapid cooling. Some imperfect separation was possible.

*Glasshouse Pots—Some Notes on their Manufacture and Use*, by MR. PERCIVAL MARSON (read by Prof. W. E. S. Turner).

After suitable weathering the fireclays used as pot clays were ready for blending, mixing, and grinding. Part of the new

mined lumps of fireclay were selected and sent to the kilns for burning. When burnt, these were broken up and ground down for the grog used in the pot clay mixtures. It should not be burnt to less than 1350° C., and should be free from the faults of burning, such as black core and soft firing. The grinding and grading should also be kept within prescribed standards.

The methods of pot manufacture were noted, the author observing that pots which had been stored for two or three years, after drying, gave more regular and reliable results than new pots used shortly after drying. Reference was made to the different practices in vogue in heating up pots in the pot arch. Mention was also made of the chief faults which pots developed in the drying room, pot arch and furnace.

*The Casting Process for Glasshouse Refractories in German Glass Plants*, by PROF. KURD ENDELL, DR. PHIL. OF THE TECHNISCHE HOCHSCHULE, Charlottenburg, Berlin.

Prof. Endell considered that the casting process would give satisfactory results in practice. He was unable to present any precise experimental results on chemical resistance to molten glass, but he believed that cast pots were chemically more resistant than hand-made pots.

#### THE ROYAL INSTITUTION OF GREAT BRITAIN.

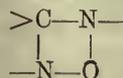
A General Meeting of the members of the Royal Institution was held on December 3, Sir James Crichton-Browne, Treasurer and Vice-President, in the chair. It was announced that the Managers had elected Mr. Joseph Barcroft, F.R.S., Fullerman Professor of Physiology, in succession to Sir Arthur Keith. The special thanks of the members were returned to Dr. Rushton Parker for his donation of one hundred pounds towards the improvement of the Library. M. le Duc de Broglie, Dr. C. L. Guillaume and Professors Debye, Einstein, Groth and von Laue were elected honorary members of the Institution. Miss Day, Mrs. Grimsdale, Mrs. King, Miss Moller, Mrs. Tipplinge, Sir George Bellby, Colonel Hippisley, Sir Alfred Hopkinson, Sir Richard Paget, Dr. J. H. Jeans, F.R.S., Professor Arthur Smithells, F.R.S., and Messrs. A. S. C. Ackermann, F. H. Hargrove, H. M. Hubbard, F. L. Lawson-Johnston, M. Manaberg, E. B. Michell, A. Muller, B. J. Orsman, and G. Shearer were elected members.

#### THE CHEMICAL SOCIETY.

Papers read at the Ordinary Meeting, December 6:—

*The additive formation of four-membered rings. Part III. A system of Nomenclature for Heterocyclic four-membered Rings, and the formation and properties of some Derivatives of -methylene di-imine-oxide*, by C. K. INGOLD.

Four-membered ring formation by the additive union of double bonds is found to be general. The variety of new heterocyclic ring-types produced from the five types of double bond studied (C:C, C:N, C:O, N:N, N:O), is such as to call for a definite scheme of nomenclature. One object of these investigations was to discover which types of four-membered heterocyclic ring were the most stable. It has been shown that certain azomethines tend to pass into stable ring bimerides. There is also evidence that many nitroso-compounds pass into stable ring bimerides. Hence, if an azomethine and a nitroso-compound of the types referred to be placed together, they should unite, giving a ring in which 2 N-atoms are united to a C- and an O-atom. Experiment shows that the ring obtained in this way has the structure



It is quite stable at ordinary temperatures. Its constitution has been established by alternative synthesis, and by a study of its decomposition at a higher temperature.

*The Dependence of Polarisation-overvoltage on Hydroxyl and Hydrogen Ion Concentration. Part I. Polarisation-overvoltage of an Antimony Cathode in Aqueous Alkaline Solution*, by H. J. S. SAND and E. J. WEEKS.

The overvoltage,  $\omega$ , of an antimony cathode in alkaline solution is found to obey the empirical equation:  $\omega = a - 2h$  ( $h$  is the potential difference between a standard electrode and a hydrogen electrode in the solution examined, and  $a$  is a constant depending only on temperature). This result, as well as the spontaneous formation of gas-bubbles, may be explained by the assumption that an ion  $H(OH)_2^+$  exists which has a definite supersolubility limit. When a sufficient number of these ions have assembled to produce the energy necessary for the formation of a gas-bubble, they decompose simultaneously (explode).

*Stereoisomerism and Local Anaesthetic Action in the  $\beta$ -eucaine Group. Resolution of  $\beta$ - and iso- $\beta$ -eucaine*, by HAROLD KING.

$\alpha$ - and  $\beta$ -vinylidiacetonalkamines on benzylation yield O-benzoyl derivatives. Benzoyl  $\alpha$ -vinylidiacetonalkamine is the local anaesthetic  $\beta$ -eucaine, and it is proposed to call benzoyl  $\beta$ -vinylidiacetonalkamine, iso- $\beta$ -eucaine. The two were resolved by camphorsulphonic and bromocamphorsulphonic acid respectively. The resolution of  $\beta$ -eucaine was effected within the transition interval where the partial racemate dl- $\beta$ -eucaine d-camphorsulphonate is the most stable form, whilst in the case of iso- $\beta$ -eucaine, the salts being of approximate equal solubility, separate alternately from the solution on fractional crystallisation.

*$\beta$ -Alizarin. An Isomeric Form of Alizarin*, by ALBERT GREEN.

When alizarin is boiled with thionyl chloride to complete solution, and the solvent is evaporated, a light brown solid is formed. Recrystallisation from glacial acetic acid and then from benzene or alcohol yields yellow needles, m.p. 195-7°. The light brown solid fumes in air, owing to decomposition of adhering thionyl chloride, and yields alizarin.

Analyses and molecular weight determinations of the yellow substance indicate the formula  $C_{14}H_8O_4$ .  $\beta$ -Alizarin is converted into alizarin by boiling with alcoholic solutions of hydrogen chloride, hydrogen bromide, or hydroxylamine hydrochloride. The same result is obtained by pouring its solution in concentrated  $H_2SO_4$  into water or ether, or by acidifying its solution in aqueous sodium hydroxide. Bromination gives 3-bromo-1.2-dihydroxy anthraquinone. Boiling for six hours with acetic anhydride  $\beta$ -alizerin gave pure diacetyl alizerin. Alizerin gave an impure product after 16 hours' boiling. Since 1-hydroxy anthraquinones are alkylated only with difficulty, while the ethers of 2-hydroxyanthraquinones are easily prepared, the former may have an o-quinonoid structure.

*The Isomerism of the Oximes. Part XV. The supposed Fourth Benzildioxime*, by O. L. BRADY and F. P. DUNN.

The authors have failed to obtain any evidence of the existence of a fourth benzildioxime.

*The Alternation in the Heats of Crystallisation of the Normal Monobasic Fatty Acids*, by W. E. GARNER and F. C. RANDALL.

The following values for the heats of crystallisation for fatty acids have been obtained:—lauric, 43.73; undecic, 32.20; capric, 38.86; nonic, 30.54; caprylic, 35.44 cal/gm. The heat of crystallisation of an odd acid is lower than the mean for its neighbours in the series, and the heat of crystallisation curve resembles the melting point curve for these acids. These results throw light on the causes of alternation in the physical properties of organic substances with long chains.

The odd acids, undecic and nonic, crystallise in two enantiotropic forms,  $\alpha$  and  $\beta$ , and the heat of transition of these have been found to be 9.89 and 8.39 cal/gm. The heat of crystallisation of the  $\beta$ -forms of the odd acids lie slightly above the curve for the even acids, thus giving an example of inverse alternation. The results are in agreement with the view that the even acids are more closely related to the  $\beta$  than to the  $\alpha$  forms of the odd acids. The differences between the heats of crystallisation of the higher members of the odd and even acids may be ascribed to differences in the mode of attachment of the carboxyl groups in the crystal molecule.

ORDINARY SCIENTIFIC MEETING, THURSDAY, DECEMBER 20, 1923, AT 8 P.M.

The following papers will be read:—

*The Relation between the Glow of Phosphorus and the Formation of Ozone*, by W. E. DOWNEY.

*The Origin of Mutarotation and the Mechanism of Isomeric Change. A Reply to Baker, Ingold and Thorpe*, by T. M. LOWRY.

*The Action of Inorganic Haloids on Organo-Metallic Compounds*, by F. CHALLENGER and F. PRITCHARD.

*Organo-Derivatives of Bismuth. Part VII. Iodo- and Nitro-Derivatives of Triphenylbismuthine*, by J. F. WILKINSON and F. CHALLENGER.

#### THE FARADAY SOCIETY.

GENERAL DISCUSSION ON "ELECTRODE REACTIONS AND EQUILIBRIA," NOVEMBER 26.

(Continued from Page 365.)

*The Gas Film Theory of Overvoltage*, by N. V. S. KNIBBS.

The theory which attributes overvoltage to a film of gas on the electrode affords an-

other instance of a discredited theory which is essentially correct.

Suppose a metal, the surface of which is free from adsorbed gas, to be made cathode in dilute sulphuric acid, any suitable anode being used. It is known that even with a very low cathodic potential a considerable current passes for a very short time, followed by a slight "residual" current. This pulse presumably occurs because the electrode is free from electromotively active hydrogen. Once current has passed the electrode becomes, in effect, a hydrogen electrode, and only the residual current (replenishing the hydrogen which diffuses away) passes until the cathodic potential exceeds that of the hydrogen electrode. A point that it is here desired to make is that the hydrogen in some way must cover the metal surface, and it seems natural to conclude that it is adsorbed to the surface. Now, suppose the potential to be increased until visible gas formation begins. What is the mechanism by which the ions are discharged and evolved as gas bubbles?

Rideal maintains that the hydrogen ions must be adsorbed to the electrode in order that they may be discharged. The discharged ions (atoms) then unite to form molecules which are still adsorbed but which evaporate at a definite rate into the electrolyte or into any neighbouring gas bubble. Except at platinised platinum and similar surfaces this rate is equivalent to only a minute current density and therefore at any ordinary current density the ions must perform the work of desorbing the hydrogen molecules before they can discharge. The energy of desorption is held to be equivalent to the overvoltage.

Some investigators maintain that the discharged ions form molecules which pass into solution in the electrolyte forming supersaturated solutions. Others assume that the monatomic hydrogen formed by the discharge of the ions accumulates on the electrode owing to the finite velocity of the reaction:  $2H_1 = H_2$ . Another suggestion is that a compound of the metal with hydrogen is formed either as an intermediate compound or as a side reaction.

Regarding the supersaturated solution theory the question arises as to why such a solution (which must be of high supersaturation) to explain even the lowest overvoltages) is formed when the hydrogen molecules could attach themselves to the electrode or pass into the gas phase immediately. No adequate reasons have been

given. The monatomic hydrogen theory postulates that the magnitude of the overvoltage depends on the concentration of monatomic hydrogen, but the latter will vary with the current density in a manner easily calculable and the actual variation differs from that calculated. The metal hydride theory has the disadvantage that no such compounds are known, and there seems no reason why they should form.

There can be little doubt that the hydrogen atoms or molecules will be adsorbed to the surface, but once all spaces are occupied the nature of the process becomes more open to conjecture. It is not easy to picture the process of the ion ejecting the molecule from the surface, as postulated by Rideal. One rather pictures the ions crowding on top of the molecules and tending to inhibit desorption.

No mention has yet been made of anodic overvoltages, and until further measurements have been made speculation is not very profitable. Even the recent measurements of Knobel, Caplan, and Eiseman are not of much assistance. Halogen overvoltages seem to increase almost proportionally to the current, and except on graphite do not reach high values at the current densities at which measurements have been made. It is unlikely that the conditions which obtain with gases of low solubility such as hydrogen and oxygen are reached at any reasonable current density with such a highly reactive and soluble gas as chlorine. All investigators agree that oxygen overvoltages are much more variable than those of hydrogen and reproducible results are difficult to obtain. This may be due to the formation of actual oxide films, not always visible, on the anodes. In general, oxygen overvoltages seem to be higher than the hydrogen overvoltages at the same metals, due, perhaps, to the greater affinity of the metals for the former gas.

#### *The Influence of Obstructive Films on Anodic Processes*, by ULICK R. EVANS.

The anodic attack of a metal proceeds readily when the product is *soluble*, or even when it is *insoluble but non-adherent*; but an *adherent insoluble* film may interfere with further attack of the anode, and may even (if non-conducting) produce valve-action. The degree of adhesion of the film depends partly on considerations of interfacial energy; but the substance is more likely to be adherent if it is the *direct product of anodic attack*, than if it is produced

by precipitation at a small distance from the anode surface. Passivity is probably due to a layer of attached oxygen atoms (or half-discharged oxygen-rich ions); it may be regarded as an oxide-film, but is not identical with any oxide known in the massive state. Any treatment which tends to scrape off, reduce, dissolve or loosen this oxide tends to remove passivity. The oxygen atoms do not merely offer mechanical obstruction to electrodic dissolution, but causes a permanent or temporary shift in the potential at which equilibrium between the metal and its ions is established after current has ceased to flow; this is best explained by supposing that the attachment of oxygen atoms reduces the "active mass" of the metal, whilst leaving that of the ions unchanged. "Degrees of passivity" are possible, and one often meets with metallic specimens which are "partially passive."

Most metals of the "A" groups of the Periodic Table appear to be permanently passive; although these elements cannot—in general—be obtained by electrodeposition from aqueous solution, the metals have a simulated nobility, due to an adherent oxide-film (tantalum, tungsten, etc.); past experiments which claim to determine the reversible "electrode potentials" of such metals require—in some cases—a different interpretation. Likewise in the transition elements (iron, nickel, platinum, etc.), there seems to be a gap between the deposition-potential and the dissolution-potential, and this causes many apparent anomalies. Disagreement even still prevails as to whether iron should stand above or below cadmium in the Potential Series.

*Studies in Heterogeneous Equilibria.* Part II.—*The Kinetic Interpretation of the Nernst Theory of Electromotive Force*, by J. A. V. BUTLER, M.Sc.

The Nernst theory of the electrolytic P.D. of metals is developed on kinetic grounds, and a kinetic deduction of the Nernst equation is given. Values of the electrode potentials calculated in accordance with the equations are at least of the right order of magnitude. The Nernst conception therefore gives an adequate and physically acceptable explanation of the facts.

*Studies in Heterogeneous Equilibria.* Part III.—*A Kinetic Theory of Reversible Oxidation Potentials at Inert Electrodes*, by J. A. V. BUTLER, M.Sc.

When an inert electrode is dipped into a solution containing two substances related

by a simple oxidation-reduction process, it usually acquires a perfectly definite and reversible electrode potential. Thermodynamically the electrical work done against this potential difference in the oxidation of one equivalent of the reduced substance at the electrode is a measure of the free energy of the process. Kinetically it may be supposed that the potential has its origin in the tendency of the more highly oxidised substance to take up electrons and that of the less highly oxidised substance to lose electrons, a transfer that occurs through the agency of the inert electrode.

It is pointed out that a metal which ionizes in two stages will contain in the solid form atoms that have lost electrons corresponding to both states. There will be a definite equilibrium between the two kinds of ions and electrons. The three processes occurring at the surface can only give rise to the same P.D. if the relative proportions of ions in the adsorbed layer are the same as in the interior of the metal. The solution which is in equilibrium with the metal is that which gives an adsorbed layer of ions in this proportion. The adsorbed layer is now identical in composition with the interior and there is no P.D. ( $E_1$ ) between the two. That is, the whole P.D. is between the adsorbed layer and the solution, and this is now the electrode potential for all three processes concerned.

A general expression was deduced, which is in accordance with the thermodynamic equation and which distinguishes the factors determining the normal potential. The relation between the (Nernst) metal potential and the oxidation potential for a metal in a solution containing its ions in different stages of oxidation, was discussed.

*Irreversible Electrode Phenomena*, by H. J. T. ELLINGHAM and A. J. ALLMAND.

The occurrence of any process with finite velocity necessarily involves more or less irreversibility. In the case of an electrochemical reaction proceeding at given finite current density, the extent of the irreversibility under given conditions is indicated by the deviation of the potential of the electrode at which it is occurring from the corresponding equilibrium potential of the reaction. Thus the degree of irreversibility of an electrochemical reaction under various conditions may be conveniently summarised by curves showing the relation between the potential of the electrode and such variables as current density, time, temperature, etc.

The polarisation due to concentration

changes in the surface layers of the electrode generally cannot be estimated. It may vary from zero in a case where the electrode neither furnishes reactants the removal of which can change its composition, nor dissolves resultants of the reaction to any appreciable extent; to values which may be very large owing to slow rates of diffusion or low velocity of chemical reactions in solid solutions. The magnitude of the polarisation due to concentration changes in the boundary layer of the electrolyte, can, however, generally be computed approximately from the known diffusion coefficients of substances in solution and an estimated value of the thickness of the layer in which the concentration gradient is established. Polarisation of this kind which is usually known simply as "concentration polarisation" is generally small owing to the relatively high rates of diffusion of substances in solution and the relatively high velocities of chemical reactions under these conditions. Also convection and ionic migration may assist in keeping it low. Under some circumstances, however, this type of polarisation may attain a considerable magnitude, examples of this were given.

The authors discussed irreversible phenomena at finite current densities, and at very small current densities. They then gave a theoretical interpretation of the results.

*Electromotive Equilibrium and Polarisation*, by A. SMITS.

Though the phenomena of passivity and polarisation have been known for more than a century, one has not yet agreed on their explanation.

The presence of a film of oxide produced by chemical attack or anodic solution was first thought to be the cause of the passive state (Faraday). It was completely forgotten, however, that if in the passive state such a film was present, the phenomenon of the origin of passivity was not in the least solved. Take for instance the case of iron which, when dipped into strong nitric acid, first dissolves rapidly and then suddenly dissolves no more. In which state is the iron covered by a film of oxide? Why does iron dissolve at constant temperature in a solution of ferrous sulphate anodically up to a certain current density, following Faraday's law, and why at a current density but a little higher does the potential rise and oxygen is evolved, while the iron nearly ceases to dissolve? Further, we can ask, why is the potential of iron changed in the direction of that of the noble metals when

it is dipped into a solution of a ferric salt, a change which is so large in a solution of ferric nitrate, that the iron becomes passive?

Why is this phenomenon dependent to so great an extent on temperature that, for instance, iron dipped into a solution of 0.14 gr. mol.  $\text{Fe}(\text{NO}_3)_3$  per litre, remains active above  $34^\circ$ , but becomes passive immediately below  $31^\circ$ , and why have traces of halogen salts such an enormous influence on all these phenomena?

From this it follows that the cause of the phenomenon cannot be a film of oxide, but that it lies deeper.

Whatever be the final state of the metal; whether there be a film of oxide or something else, the primary phenomenon is that of passivity itself. At first, and indeed, even until quite lately, this was not generally understood.

All later theories have this in common that they assume as the cause of passivity the retardation of some process or other, which goes on when a metal is dissolved or precipitated. These theories can therefore be called *velocity-theories*, and they can be divided into the following groups:—

1. Theories which assume the formation of oxides as a result of a retardation.
2. Theories in which the cause of passivity is ascribed to the formation of an oxygen-charge or of a metal-alloy.
3. Theories in which hydrogen acts as an activating agent (Grave, Adler, Rathert).
4. Theories combining the hydrogen- and oxygen-charge hypothesis (Foerster).
5. Hydration-velocity theory (Leblanc).
6. Valency theory (Finkelstein, Müller).

Evidence, based on the study of the influence on the potential difference of small quantities of mercury dissolved in aluminium, is brought forward in support of an explanation based upon catalytic influence.

#### CORRESPONDENCE.

*To the Editors of THE CHEMICAL NEWS.*

SIRS,—From time to time the non-technical journalist supplies, in all good faith, misleading information, and I fear that it is seldom possible to catch up with items of news which are widely circulated and which contain statements of dubious accuracy.

A paragraph recently circulated and quoted by the Technical Press refers to a violent explosion which set fire to and sank the British steamer "Otterburn." The paragraph concluded by saying that the

disaster was thought to be due to the explosion of barrels of chlorate of potash. I am informed, on what appears to be quite good authority, that there was no chlorate of potash on board the ship, but that there was a parcel of chloride of potassium.

The transport of dangerous substances is always a matter of difficulty, and it is therefore desirable that one should not unwittingly increase the difficulties by blaming a dangerous substance unnecessarily. To weigh down the statistics of explosions due to chlorate of potash by such items of news as that to which I refer would be misleading and prejudicial to those firms who have to send abroad such goods.—Yours, &c.,

W. J. U. WOOLCOCK,  
General Manager.

The Association of British Chemical  
Manufacturers.

166, Piccadilly, London, W.1.

December 3, 1923.

#### NOTICES OF BOOKS.

*The Electron in Chemistry*, by SIR J. J. THOMSON, O.M., F.R.S. Pp. V. + 144 (with index). Messrs. J. B. Lippincott Company, Philadelphia, Penn. 1923. Price \$1.75.

This book embodies the five lectures Sir J. J. Thomson delivered before the Franklin Institute in April, 1923; and it contains much new matter which Prof. Thomson had himself contributed to the subject of the electron in chemistry, etc., which had appeared in the *Philosophical Magazine* and elsewhere.

The main subjects dealt with are:—Arrangement of electrons in atoms; stability; periodic law; allotropic form; atomic size; ionisation potential; specific inductive capacity of gases; molecules; electron theory of valency; arrangement of electrons in octets; chains; chlorides, carbonates, etc.; residual affinity; molecular compounds; Werner's theory; electrolytic dissociation; mechanism of combinations; condensation on surfaces; double electrical layers; active molecules; Thiele's theory; Keto-enol change; production of light; homologous elements; variable valency; paramagnetism; diamagnetism; solids; crystals; vibration of electrons in crystals; compressibility; surface tension; intermetallic compounds, &c.

Of particular value is the bringing out of certain atomic and molecular attributes as due to the behaviour of electrons as revealed by positive-ray experiments and other phenomena, in connection with

which Prof. Thomson is a pioneer investigator. The following are a few interesting features.

The proposed law of force between a positive charge and a negative electron is shown to lead to electrons in positions of stability round a nucleus without describing orbits round it.

The cubical theory of atoms and twisted cubes are discussed, but the latter is not drawn.

On page 3, Prof. Thomson says: "As up to the present nothing has been discovered that cannot be resolved into electrons and positively electrified particles, it is natural to frame a theory of the structure of the atom on the supposition that it is built up of these two ingredients. It should be borne in mind, however, that our means of detecting the existence of electrically charged bodies far surpass those for detecting uncharged ones, and if there were any uncharged constituents of the atom, they would in any case probably have escaped detection. We know, however, that even supposing such constituents do exist, their mass must be negligible compared with that of the positive parts, for these parts account for well within a fraction of a per cent. of the whole mass of the atom."

On page 26 it is pointed out "that on passing from one period to the next, the volumes of all the atoms are increased in the same proportion," thus:—

F = 1.35 A units in diameter.

Cl = 2.10

O = 1.30

S = 2.05; &c.

Then, by comparison:

Cl/F = 1.55.

S/O = 1.57; &c.

In the section (see page 39) dealing with combinations of different elements, it is noted that Thomson distinguishes between the molecule of carbon monoxide (CO) and that of the carbonyl radicle (CO). In the latter it is suggested that two out of the four electrons of the carbon atom have united with the oxygen to make up the octet, while the other two are free to join up with other electrons. In the same way there are two NO's.

On page 105, Prof. Thomson says of oxygen: "The most fascinating of all magnetic bodies is, to my mind, oxygen. Here we have one of the simplest of atoms; its atom contains only eight electrons, it is a gas, and therefore in the simplest of all physical states, and yet it alone of all gases is paramagnetic, and quite strongly so. An-

other remarkable thing about it is that innumerable as are the compounds of oxygen, there is only one, NO, into which oxygen carries its magnetic properties. This would seem to suggest that the magnetic quality does not arise from some quality intrinsic to the atom, but from some speciality in the arrangement of the colligating electrons in those molecules where it exhibits its magnetic character. The oxygen molecule itself is the most conspicuous example; the arrangement of the electrons may be represented symbolically as two cubes having a face in common, this face being at right angles to the line joining the atoms. If the system were rotating about this line there would be an odd number of square faces in rotation. A rotating square with its electrons would act like a current and thus behave like a magneton. Now, suppose that the rotation of electrons must be such that adjacent squares rotate in opposite directions, and it is evident that if we start one from rest in one direction, the adjacent one will start in the opposite direction. Suppose, then, that the electrons in the planes of the squares were rotating so that the rotation in one plane is opposite to that in the adjacent plane, then two of these planes will be rotating in one direction and the third in the opposite, the resulting magnetic effect will be the same as if only one plane rotated, and this will produce a magnet of finite moment."

The above statement may be clear to some readers, but we think that a diagram showing the rotations would have been helpful in this case.

Paying tribute to Prof. Richards' work in respect of the compressibility of the elements, Prof. Thomson gives some calculations of the compressibility of metals based on the supposition "that they are made up of cubical cells with an atom and one-eighth of an electron [not, of course, a fractional electron] at each of its eight corners, each cell corresponding to an atom with its electron." This leads to a formula for  $k$ , the compressibility being  $1/k$ , which is—

$$k = (3.65/9)e^2 (\Delta/M)^{4/3}$$

$e$  = charge of an electron;

$M$  = mass of an atom;

$N$  = density of the solid;

$\Delta$  = density.

For example, lithium is—

$\Delta = 0.534$ ;

$k = 0.14 \times 10^{12}$  calculated by above formula;

$k = 0.114 \times 10^{12}$  as observed by Richards. Developing the subject further, in the

case of the diamond  $1/k = 0.178 \times 10^{-12}$ , which agrees closely with the recent value of Adams (*Washington Acad. Sci.*, 1921, XI., p. 45),  $0.16 \times 10^{-12}$ .

Prof. Thomson's book is rich in suggestive ideas, and it should be widely read. There is only one feature in respect of its get-up which we think could have been improved, and that is to have introduced a recapitulation at the end of each section or chapter, so that the reader would know where he stood in matters which may seem rather confusing, especially to those not steeped in the subject. The printing and binding is up to the high standard of book production as set by the most progressive publishing houses.

## New Patents.

This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

### *Latest Patent Applications.*

206229—Chance & Hunt, Ltd., Calder, W. A. S., and Palmer, W. H.—Process for condensing the acid fumes evolved during the concentration of sulphuric acid.

186589—Hansgirt, Dr. F.—Process and apparatus for the extraction of zinc from zinciferous materials.

29313—Chemische Fabrik in Billwarder vorm., Hell & Sthamer Akt-Ges.—Manufacture of pure anthracene and carbazol. Nov. 20.

### *Specifications Published this Week.*

206671—Stacey, F.—Electric apparatus for the production of peroxides of nitrogen.

206711—Lacy, S. A. De.—Frame to make possible, in the same apparatus, solvent recovery by distillation after extraction of a substance has been made by that solvent.

201914—Krupp Akt-Ges., F.—Articles requiring a high resistibility against corrosion by ammonium chloride solutions.

### *Abstract Published this Week.*

204886—Chromium oxide and salts; chromates; barium chloride.—Chemische Fabrik Griesheim-Elektron, of 51, Gutleutstrasse, Frankfurt-on-Main, Germany.

*Alkali chromates; chromium oxides and salts; barium, chromium, and iron chlorides.*—Chrome iron ore is converted into ferrochromium in the known manner, the ferrochromium is dissolved in hydrochloric acid, and the chromium precipitated as hydrated oxide by calcium or barium carbonate. The precipitate is separated and used to produce alkali chromate or chromium salts. The filtrate, if barium carbonate was used, is evaporated and cooled to separate barium chloride, and the mother liquor may be evaporated to obtain ferrous chloride. In the precipitation of the chromium hydrate it is preferred to use granular limestone or witherite and hot chloride solution.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.



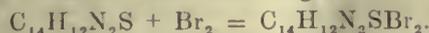
## THE CHEMICAL NEWS,

VOL. CXXVII. No. 3323.

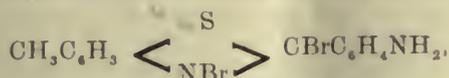
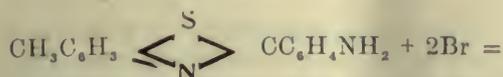
## 4' AMINO 1 PHENYL 5 METHYLBENZOTHIAZOLE AND ITS BROMINATION IN GLACIAL ACETIC ACID, THE DIBROMO PRODUCT OF GATTERMAN AND THE FLUORESCENCE OF SOME BENZOTHIAZOLES.

BY R. F. HUNTER, F.C.S.

Gatterman, during his researches on 4' amino 1 phenyl 5 methyl benzothiazole, observed that when the base is dissolved in glacial acetic acid and brominated, it adds two bromine atoms according to:



Anschutz and Schultz, while working in the same field, observed the formation of similar compounds in the cases of the dehydrothioylidins. We should expect the reaction observed by Gatterman to be:



that is to say to consist in the normal splitting of the double bond and the addition of bromine at the nitrogen and carbon atoms. The objection to this which has been raised is that in the above structure we have a bromine atom attached to a nitrogen atom directly, and that the compound should be very unstable and therefore tend to resemble nitrogen bromide in properties and stability to a certain extent. Whereas the compound is known to be quite stable at ordinary temperatures. It was therefore decided to prepare this compound and examine it. A further point to be observed is that if the interpretation given to the reaction is correct, then this reaction should be a general one and apply to all substituted benzothiazoles of this class. The recent researches which have been carried out on the derivatives of the base show that these brown products are formed whenever the thiazole is dissolved in glacial acetic acid and brominated in the manner described in the experimental part of this paper, some of the results have been communicated to the

transactions of the Society of Chemical Industry, and a good many are as yet unpublished. Another point which was noticed during the investigation of these compounds was the remarkably fine fluorescence which some of them display in solution. This has been noticed previously by various workers. The effect is remarkably good when the substances are placed under the action of the ultra violet rays of a mercury lamp. Three derivatives were examined in this manner: the base itself in alcoholic solution, the acetyl derivative, and the dibromo product. The last two were used in the form of their solutions in acetic anhydride and glacial acetic acid respectively.

## EXPERIMENTAL.

The 4' amino 1 phenyl 5 methylbenzothiazole used in the experiments was prepared by the method described some time ago (*Trans. Soc. Chem. Ind.*, 1923, XLII., 302). The product was recrystallised from alcohol in the manner described in the original paper.

*Dehydrothioparatoluidine Dibromide*.—1 gm. of pure base is dissolved in 20 to 30 ccs. of pure glacial acetic acid in a 140 cc. beaker. Excess of bromine, according to the theoretical equation given above, is then added drop by drop from the burette containing bromine; the solution in the beaker is kept well stirred during the bromine addition; about 2 ccs. of bromine are added altogether. The first drop of bromine produces an immediate precipitate, which is of a dark red-brown in colour. The solution is then allowed to stand for twenty minutes, and then drowned in water (about 100 ccs. of cold water being added for complete precipitation). The precipitate is allowed to stand for a minute or two and then filtered, washed for some time with hot water and then with alcohol, dried, and then weighed. Yield, 1.3 gm.

The product, when dry, is a chocolate powder, as prepared above. It is soluble, as most of these compounds are, in xylene and in acetic acid. It was thought that it might be possible to diazotise the dibromo compound, and couple this with suitable couplers to form azo dyes, though such dyes would be rather unstable. Some of the compound was therefore dissolved in acid, and sodium, nitrite, nitrous acid, however, was found to split off bromine, the odour of bromine being quite distinct. Nitrous acid was also found to have a similar effect on the dibromo compound of benzaldehydo-

thioparatoluidine, which was also examined.

*4' amino 1 phenyl 5 methyl benzothiazole.* A solution of the base in alcohol was exposed to a mercury lamp; the solution exhibits a beautiful green fluorescence.

*The Dibromo product.*—This was examined in a similar manner, using a solution of the substance in glacial acetic acid. The fluorescence was a beautiful blue

colour. The introduction of the bromine atoms shifts the colour from the red end of the spectrum to the violet end.

*4' Acetyl amino 1 phenyl 5 methylbenzothiazole.*—A solution of this in acetic anhydride gave a bright, strong fluorescence.

*The Imperial College of Science  
and Technology.*

September, 1923.

## ARE THE NATURAL GROUPINGS OF THE ELEMENTS AND THE SPECTRAL LINES OF HYDROGEN RELATED?

### PART VII.

By F. H. LORING.

In further development of this study—see *The Chemical News*, 1923, CXXVII., pp. 225, 257, 273, 290, 337, 355, 369—attention is here drawn to an extension of the direct relations between the *group numbers* derived from the five Balmer lines and the distances of the various satellites from their respective planets.

In the main part of this investigation the planets Uranus, Jupiter, and Saturn will be dealt with, as these planets are particularly rich in satellites; and they consequently afford a range of values with which to test further the significance of the relationships thus far revealed for the first time, so far as the writer is aware.

The accompanying tabulations show the results of these findings, and they need no special explanation, except to state that the values under the letter C were obtained from a drawing given in the *Encyclopædia Britannica* (Planets), which gives the *relative* distances in an arbitrary scale. This was a desirable precaution to take at the outset, partly as a rough check against the other values obtained from Chambers' "Handbook of Astronomy" (1889), Vol. I., which are used here. Of course, the values (C) are only approximate.

It is important to specify all distances in terms of a common unit, in this case miles, M, so that the same reducing constant (K) can be used for each planetary system. S is the name of the satellite. N is the result of dividing M by K, while the corresponding group numbers derived from the Balmer lines are indicated by the letter B. D is the difference.

#### URANUS.

	S	C	M	K	N	B	D
1st Ariel	.....	(6.4)	124,700	19,310	= 6.46	7	+0.54
2nd Umbriel	.....	(8.9)	173,900		= 9.00	9	0.00
3rd Titania	.....	(14.3)	285,300		= 14.77	13	-1.77
4th Oberon	.....	(18.5)	381,600		= 19.76	21	+1.24
		(+0.54) + (+1.24) = (+1.78)					which balances (-1.77).

It will be seen that in the case of this planet, the satellite distances agree very closely indeed with the B values.

With regard to the derivation of the constant (K), if  $\Sigma M$  represents the sum of the satellite mean distances, and  $\Sigma B$  represents the sum of the group numbers (B), then  $\Sigma M/n$  ( $n$  being the number of satellites, in this case 4) divided by  $\Sigma B/n$  ( $n$  being the number of group numbers, also 4), gives the constant K here employed for systematically reducing all satellite distances to a set of comparable figures. This calculation, based upon the Uranus values, gives the

constant (K), which is applicable also to the satellites of Jupiter and Saturn, though in the latter case there appears to be a systematic error in respect of Rhea and Titan; but this may be due to the attempt to extend the Balmer values rather than develop the Paschen, or even the Lyman or Brackett, series (see Note 4 in Part VI. of this paper). In the instance of satellites much nearer to their planet (Mars) than any here shown, the Lyman series may give the proper values, but the examples are not numerous enough to afford a test that is so convincing as those being dealt with here.

JUPITER.

	S	C	M	K	N	B	D
1st	Io .....	(13.5)	267,300	19,310	= 13.84	13	-0.84
2nd	Europa .....	(21.0)	425,100		= 22.01	21	-1.01
3rd	Ganymede ....	(34.1)	678,900		= 35.12)	*	
4th	Callisto .....	(57.2)	1,192,800		= 61.72)	48	

\* Mean = 48.42, giving D = (-0.42). A mean error for all the values is (-0.76), which is very satisfactory.

It should be noted that the first two terms of the series are absent in this case, as the relations do not indicate whether the

lacunæ, so to speak, will or will not contain satellites, very much as with elements in the case of the periodic table.

SATURN.

	S	C	M	K	N	B	D
1st	Minas .....	(6.0)	115,100	19,310	= 5.95	—	—
2nd	Enceladus ....	(8.0)	147,750		= 7.65	7	-0.65
3rd	Tethys .....	(10.0)	183,000		= 9.46	9	-0.46
4th	Dione .....	(13.3)	234,400		= 12.14	13	+0.86
5th	Rhea .....	(18.6)	327,300		= 16.95	21	+4.05
6th	Titan .....	(42.5)	758,700		= 39.30	—	—
7th	Hyperion .....	(54.0)	916,700		= 47.48	48	+0.52
8th	Iapetus .....	(124.5)	2,221,100		= 115.02	—	—

See remarks above *re* Rhea and Titan.

If, now, all the foregoing values corresponding properly to numbers 7, 9, 13, 21, 48, be grouped and averaged, the following results are obtained:—

(6.46 + 7.65)/2	= 7.05
(9.00 + 9.46)/2	= 9.23
(14.77 + 13.84 + 12.14)/3	= 13.58*
(19.76 + 22.01)/2	= 20.88
(48.42 + 47.48)/2	= 47.95

\* The moon's distance from the earth when reduced by the constant, K, gives the value 12.37. Averaging this value with 13.58 gives 12.97, which is practically 13. Then  $\Sigma N = \Sigma B$ .

Considering the wide range of phenomena represented, there seems to be no doubt whatever that the relations thus indicated in this series of papers are significant of some important law of far-reaching consequences; but it must be remembered that these studies are only first efforts in a new line of investigation.

SUMMARY.

In this paper it is shown that the distances from the satellites of Uranus, Jupiter, Saturn and the Earth follow a planetary displacement law represented by the numbers 7, 9, 13, 21, 48, which are derivable directly from 5 Balmer lines of the hydrogen atom spectrum, or from the 5 groupings of the periodic

table of the chemical elements. These numbers also agree with the radial distances of 5 consecutive planets, measuring from the sun, counting the asteroids collectively as one member of the system. The question is raised as to whether one of the other line-series will likewise afford other values for the satellites much nearer their planets than those harmonised by this study, and also incidentally harmonise the irregularity in the case of Rhea and Titan. It is to be noted that there are 9 planets in the solar system, counting the asteroids collectively as one, so that some further development of one or the other of these series is to be expected, as the Balmer series only agrees with 5 members. *The point to be made, however, is that the values above given agree in many consecutive instances over a range of natural phenomena of almost incredible magnitude.*

NOTES.

Other Satellites:

Earth—

1 only. Moon. 238,900/19,310 = 12.37\*  
\* Near to the value 13.

Neptune—

1 only. Lassell. 223,000/19,310 = 11.54\*  
\* Mean between 9 and 13; but may belong to another series. Chambers mentions that this satellite is peculiar in its movement. It, of course, belongs to the most distant planet.

*Mars*—

1st Phobos 6,000) See remarks above  
2nd Deimos 15,000) *re* other series.

*Saturn*—

The Balmer  $\zeta$  line, by the formula, p. 291, gives 5.6, which is near to the value above for Mimas: 5.95. 62.5 may be used as a dividing constant instead of 61.5 for the whole series. A more recently-discovered satellite of this planet (Phoebe) has the probable *comparative* values as follows:—

$$7,798,300/19,310 = 403.83^*$$

\* This is outside the present range of calculations, and it would seem to involve another series as indicated above.

*Jupiter*—

A more recently-discovered satellite of this planet has the probable *comparative* values as follows:—

$$109,160/19,310 = 5.65^*$$

\* Averaging this figure with that of Mimas, 5.95, gives 5.80, the theoretical value being about 5.6.

These distances here are also in miles, as given above in the case of Uranus, &c.

### DYESTUFFS (IMPORT REGULATION) ACT, 1920.

#### APPLICATIONS FOR LICENCES IN NOVEMBER, 1923.

The following statement relating to applications for licences under the Dyestuffs (Import Regulation) Act, 1920, made during November, has been furnished to the Board of Trade by the Dyestuffs Advisory Licensing Committee.

The total number of applications received during the month was 612, of which 485 were from merchants or importers. To these should be added 8 cases outstanding on November 1, making a total for the month of 620. These were dealt with as follows:—

Granted—433 (of which 413 were dealt with within 7 days of receipt).

Referred to British makers of similar products—119 (of which 105 were dealt with within 7 days of receipt).

Referred to Reparation supplies available—40 (all dealt with within 2 days of receipt).

Outstanding on November 30, 1923—28.

Of the total of 620 applications received, 558, or 90 per cent., were dealt with within 7 days of receipt.

## GENERAL NOTES.

## ATMOSPHERIC CORROSION OF METALS.

Future generations will express astonishment that right into the twentieth century we have been content to extend the use of constructional materials, without apparently giving any consideration to their relative corrodibility.

A small committee which could marshal the available scientific knowledge and apply the simplest of business costing principles, would almost certainly effect extraordinary changes in the choice of materials for building, public works, and innumerable engineering purposes. Much too little attention is usually paid to upkeep expenses in relation to initial cost of installation.

Comparing two metals, for instance; in the one case the initial cost may be less, but after the painting, repainting, repairing and perhaps even replacement are added, it may frequently prove much less economical than a second metal which can be used without any protective coating whatever.

The real problems of corrosion and their solution cannot, of course, be solved in this way, since much more fundamental knowledge of the causes and sequence of effects is required.

There seems to be no doubt that still greater advances in the choice, treatment, and use of materials, from the point of view of their resistance to corrosion, will result from systematic observation and experiments.

One of the most important researches on the subject is that being carried out by the Atmospheric Corrosion Committee of the British Non-Ferrous Metals Research Association. Mr. W. H. J. Vernon, B.Sc., the investigator, has just submitted his first experimental report, which was read before the Faraday Society in London on Monday, December 17. The work described has been carried out under the supervision of Professor H. C. H. Carpenter, F.R.S., at the Royal School of Mines, and dealt chiefly with the initial stages of corrosion—the tarnishing of metals. Quantitative measurements have been made on the relative behaviour of different metals and alloys, both indoors and outdoors. The subject is of immense importance, not only to those who are concerned in the manufacture of metal fittings and articles, but in its direct relation to labour-saving in daily housework.

The investigation was by no means confined to tarnishing, which formed the outstanding feature of the first report, merely because it represented the initial stage of corrosion. Exposure tests to outside atmospheric influences have been progressing since the commencement of the research, and will doubtless yield their quota of evidence in due course.

The extension of this work depends to a large extent on the support given to the British Non-Ferrous Metals Research Association for this specific purpose; the investigation already has the backing of the Royal Institute of British Architects, the Department of Scientific and Industrial Research, and many of the leading firms and associations in the metal industry.

#### THE WORLD'S WHEAT SUPPLIES AND REQUIREMENTS.

According to an estimate made by the International Institute of Agriculture, at Rome, the wheat-exporting countries are theoretically in a position to furnish to the importing countries during the cereal season from August 1, 1923, to July 31, 1924, about 570 million centals of wheat. To this quantity Canada could contribute about 221 million centals, the United States a little over 112 million, India 12 million, Argentina 122 million, Australia 55 million, while the Balkans, Hungary, Russia, and the French colonies in North Africa could furnish altogether about 45 million centals.

Estimates of probable requirements in the importing countries are not at all easy to prepare for the current season, owing to recurring difficulties presented by the financial and economic conditions existing in sundry European States and by the efforts of some Governments to limit imports of foreign wheat. In pre-war times it might generally be assumed that individual consumption in a given country would not vary much from year to year. Having ascertained the quantity produced in a certain country during a stated season, it was possible to define with fairly close approximation the quantity of wheat required to supplement home production during the twelve-month.

Now, however, the basis for such an estimate has become much less secure, and it by no means follows that a short crop entails a correspondingly larger import, or *vice versa*. There is proof of this in effect-

ing comparison between data of production and imports, for the two seasons 1921-22 and 1922-23 respectively.

Although the 1922 crops in importing countries were 110 million centals less than in 1921, these countries took, between August 1, 1922 and July 31, 1923, much the same quantity of foreign wheat. For the most part the causes leading to such a decline in consumption are still in operation. Even if the plentiful yields so general in 1923 should result, for some countries, in a larger consumption than last year's, it seems probable that import requirements between August 1, 1923, and July 31, 1924, will be on a more restricted scale than those of last season. In any event, these imports are unlikely to exceed last year's total of 430 million centals.

To sum up:—

(1) The quantity of wheat that theoretically might be despatched by the exporting countries to the importing States between August 1, 1923 and July 31, 1924, is about 570 million centals.

(2) The quantities required for the same period by importing countries to supplement their home production may reach 430 million centals at most, but it is improbable that this figure will be attained.

(3) The quantity available in exporting countries will therefore suffice to meet the requirements of the importing countries until the next harvest in the northern hemisphere, and to leave a surplus on hand at August 1, 1924. This surplus may be estimated at not less than 140 million centals.

#### DRUGS, CHEMICALS, ETC., FOR EGYPT.

The British Commercial Agent for Egypt has forwarded to the Department of Overseas Trade copies of documents issued by the Egyptian Ministry of the Interior in connection with a call for tenders for the supply of miscellaneous drugs, chemicals, etc., required by the Department of Public Health during 1924-25. The schedule of stores required includes:—

- (1) Proprietary articles;
- (2) Druggists' sundries;
- (3) Surgical dressings;
- (4) Crude drugs and heavy chemicals;
- (5) Fine chemical products; and
- (6) Galenicals and packed articles.

Tenders will be received by the Director of Stores, Department of Public Health,

Cairo, up to noon on January 14, 1924. Article 5 of the conditions of tender states that "the articles supplied must be exactly similar to the standard sealed pattern, kept at the Central Stores, Department of Public Health, Cairo, and in number, weight, and measurements in accordance with the written schedule or size roll given to the contractor by the Director of Stores. The standard pattern will be sealed by the Department and by the contractor." It is also stipulated that the tenderer must be a person residing in Egypt, or must have a representative there, and will give in his offer an address at which notices may be served upon him. The Department of Overseas Trade will furnish U.K. firms desirous of tendering and not represented locally with the names and addresses of United Kingdom merchant firms established in Egypt, who would be prepared to handle tenders on their behalf.

A copy of the schedule of stores required, conditions and form of tender, may be seen on application, while a further set of these documents is available for loan to firms in the provinces who may be unable to arrange for a London representative to call here.

#### GERMANY'S COMMERCE AND INDUSTRY DURING NOVEMBER.

Mr. J. W. F. Thelwall, H.M. Commercial Secretary at Berlin, has forwarded to the Department of Overseas Trade a review on the state of Germany's trade and industry during November.

No improvement occurred in the economic situation in November. The position in occupied territory continued hopeless. Its economic life, with a few exceptions, remained stagnant. There the possibilities of export diminished more and more, while imports of such raw materials as were formerly produced in the country increased. Unproductive work became more extensive, an exceptional rise in the costs of production occurred, and the level of prices for goods was generally very high.

##### *Mining.*

The pit-coal production in Upper Silesia was again interrupted. The small output of the preceding month was, therefore, scarcely exceeded. There was no complaint as to the supply of trucks. In spite of a reduction of advance freights by the railway and of reduced shipping rates, there were

practically no consignments to places of transshipment. The demand revived as compared with last month owing to the more pressing requirements at this time of the year of agriculture, household coal consumers and gasworks. As before, however, the orders for dust coal were not extensive.

In the Central German brown coal district the market conditions continued unfavourable, so that shifts had to be dropped in many mines, although after the last strike a fairly considerable number of workers were not reinstated. In some works the number had been reduced by 15-45 per cent. Other works had not yet started operations again after the strike.

In the Ruhr coal district all the miners and employees were given notice of termination of work on November 30 and December 31 respectively.

##### *Potash.*

In the potash industry, with the exception of a somewhat more lively export of sulphates to North America, the market was very unfavourable. Further shifts had consequently to be dropped in all the works, and dismissals had partly to be resorted to. Inland business became more and more paralysed. It is hoped, however, that after the introduction of a sufficient quantity of stable media of payment, the main difficulty in the purchase of potash salts will be overcome. The demand, particularly from abroad, for chemical by-products, was still satisfactory. In order to offer an incentive to the immediate placing of orders for potash, the Potash Syndicate, in agreement with agricultural and trade organisations, granted a goods discount to consumers. In spite of this, however, only small orders were placed on behalf of agriculture, so that, next to April, November was the most unfavourable month of this year as far as sales were concerned.

##### *Metals.*

The metal trade was at times brought to a standstill, as the position on the metal market grew continually worse. The decree, issued at the end of October, again prohibiting free transactions in foreign values and the action taken at the same time by the Reichsbank to support the mark, resulted in a very important difference between the inland and foreign mark rates. The metal trade was thereby greatly hampered, and the fixing of uniform metal prices was impossible. For this reason the Berlin Metal Exchange again ceased to issue quotations.

### *Chemical Industry.*

The general economic situation necessitated further restrictions of work in the chemical industry in occupied territory. If uninterrupted communication with unoccupied Germany is not made possible, the works must come to a total standstill. In the chemical preparations industry the demand for laboratory chemicals was very small, and that for glass chemicals diminished in the degree in which the glass-works were compelled to restrict work or close down. The demand from abroad also fell off as sale prices approached the world's market level. It is felt to be a particular burden that just at the present time the refunding of the British Reparation Levy should have been discontinued, and thus all possibility of selling German products to England removed. It is all the more to be regretted, as French competition is greatly felt in England, and will now secure the whole trade without effort. A slight revival of both inland and foreign trade in the remaining chemical preparations was reported.

### *Glass Industry.*

In the sheet glass industry there was no improvement on the inland market. The demand from abroad increased somewhat, but prices were so depressed owing to Czecho-Slovakian and Belgian competition that they scarcely covered much more than half the costs of production. Wage strikes interfered with production in the hollow-glass industry. The advance in the costs of production, which made competition abroad impossible, led to further restrictions of work and the closing down of factories.

### *Ceramic Industry.*

The position of the porcelain industry became considerably worse, and was characterised by a complete stagnation in inland sales, numerous cancellations of orders, and restriction of operations. Restricted operations were reported from the Palatinate, Wurttemberg, Thuringia, Saxony, Silesia, and Brandenburg. The electro-technical porcelain industry suffered from a great lack of orders and from short-time work. Only the glazed wall-tile factories were, in part, well employed.

### *Paper Industry.*

The degree of employment in the paper industry was, in general, not unfavourable as compared with other branches of industry. By the middle of October, however, the number of unsatisfactorily employed works which had to curtail working hours or

work for stock preponderated. Since then the position has grown considerably worse. The financial difficulties (growing costs of production, diminishing receipts owing to falling off of sales, restriction of credit and the difficulty of obtaining the latter from the banks) increased continually, and the stock of orders was reduced. According to one report from an industrial association, in land trade was practically at a standstill. The raising of even the most necessary funds for raw materials, wages and salaries, etc., met with the greatest difficulties. In order to maintain the factories, the industry is more than ever dependent on exports. In the paper producing and working up industry, the possibilities of export in general declined more and more, owing to excessively high prices. For the rest, the conditions as regards production were not unfavourable, especially for the paper raw material industry. The water conditions improved, and sufficient German coal was obtainable (the demand having fallen off in view of restrictions of work), though it was, in part, more expensive than British coal. The supply of auxiliary materials, with the exception of dyes, was adequate. The production of wood-pulp increased, but the demand was generally small.

### *Leather Industry.*

The prices of hides and skins rose considerably, owing to the further depreciation of the mark. With a few exceptions, the pre-war prices have not only been reached, but exceeded. A more wholesome demand on the part of manufacturers was recorded. The turnover would have been greater, had it not been for money difficulties. In the leather trade business was almost stagnant in the first part of the month, owing to the lack of money; but here also a more wholesome demand set in subsequently, although an important turnover could not be achieved in consequence of the difficult position as regards currency. As before, complaint was made in the boot and shoe industry as to the lack of purchasing power on the part of the public. A better turnover was, however, obtained in the retail trade.

### *Sugar Industry.*

Lively business in sugar (for consumption) from the new harvest developed in the course of the month. The reports regarding the proposed export by the Government of sugar and regarding the estimated harvest yield (the latter is estimated to be about 20 per cent. smaller than last year) called forth a brisk demand for sugar. The

factories, however, placed only comparatively small quantities on the market. The result was an increase in prices, so that inland prices have now exceeded the world's market level, although the latter has also advanced considerably. The sugar working up industry continued to complain of a strong decline in business owing to too high prices, and also, in particular, of a great shortage of sugar, so that short time work and dismissals frequently became necessary.

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE ROYAL SOCIETY OF ARTS.

On Monday, December 10, the Cantor Lecture (II.), entitled *Recent Progress in the Wool Industries*, was read by ALDRED F. BARKER, M.Sc., Professor of Textile Industries, the University, Leeds.

On Wednesday, December 12, at the Ordinary Meeting, a paper entitled *The Preservation of Historic Buildings and Ancient Monuments* was read by SIR FRANK BAINES, C.B.O., C.B.E., Director of Works, H.M. Office of Works. Sir Aston Webb, K.C.V.O., C.B., C.R.A., Vice-President of the Society, presided.

The Dominions and Colonies Section held a meeting on Monday, December 17. A lecture entitled *Empire Settlement* was delivered by WILLIAM C. NOXON, Esq., Agent-General for Ontario. The Right Hon. the Earl of Airlie, M.C., presided.

##### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

###### ORDINARY MEETING.

Held at the Chemical Society's Rooms, Burlington House, on Wednesday, December 5, 1923, Mr. P. A. Ellis Richards (President) in the chair.

Certificates were read for the first time in favour of:—Messrs. Frank Knowles, Archibald Knox, A.I.C., Charles Roger Middleton, B.Sc., A.R.C.S., D.I.C., A.I.C., Harold Richard Read, A.I.C., George Hogan, F.I.C., Thomas Francis Doyle.

Certificates were read for the second time in favour of:—Messrs. Robert Charles Frederick, Hubert Thomas Stanley Britton, M.Sc. (Lond.), F.I.C.

The following were elected members of the Society:—

Messrs. Laurence Eversley Campbell, M.Sc. (Lond.), F.I.C., John Troubridge Hannen, B.A. (Cantab.), A.R.C.Sc., A.I.C., Cyril Langley Hinton, F.I.C., Douglas William Kent-Jones, M.Sc. (Lond.), F.I.C., Thomas William Alan Shaw, M.Sc. (Liv.), William Hall Simmons, A.I.C., Kenneth Edward Nethercoate Williams, Percy Noel Williams, M.Sc. (Liv.), A.I.C.

The following papers were read:—

*The Crystalline Bromides of Linseed Oil*, by HAROLD TOMS, M.Sc., A.I.C.

The "insoluble bromide" of linseed oil, first described by Hehner and Mitchell, appears to consist of mixtures in varying proportions of two crystalline bromides, viz.: (1) a linolic-dilinolenic bromo-glyceride, and (2) the trilinolic bromo-glyceride of the oleic-linolic-linolenic bromo-glyceride. These two bromo-glycerides have been obtained in pure condition by crystallisation from ethyl acetate. They melt at 153° C. (corr.) and 117° C. (corr.), respectively. The solubility of the more insoluble bromide in ethyl acetate lies between 0.15 and 0.20 gm. per 100 cc. at 15 to 20° C. The methods of estimating the bromine in these compounds have been studied, and it is shown that theoretical results can be obtained by the method of Carius and by a modification of the method of Stephanow, but not by the lime method. Various methods of estimating the more insoluble crystalline bromides are described, the yields of the purest product varying from 9.39 to 11.6 per cent. in the case of different oils. The results obtained suggest that there is some relationship between the yield of this crystalline bromide and the iodine value of the original oil.

*The Plea for Standardisation*, by M. S. SALMON, B.Sc.

The author emphasises the fact that in every field of analytical chemistry instances are continually occurring where different, although well recognised methods of analysis yield varying results. He refers in particular to the case of dried milks, and instances one example where one sample of dried milk was sent to four well-known analysts, and a considerable divergence of figures resulted according to the methods used, particularly in the case of the fat and lactose estimations.



Referring next to essential oils, the need for standardisation is seen to be urgent, for in many cases minute modifications in detail cause substantial differences in results. The same remarks apply to the case of inorganic materials of simpler composition, and the author sees a recognition of the difficulties in the details laid down for analyses under the Fertiliser and Feeding Stuffs Act, and he strongly advocates the formation of a Committee to consider the whole question.

*A Note on the Estimation of Chromium*, by HUBERT T. S. BRITTON, M.Sc., F.I.C.

The gravimetric methods of estimating chromium as oxide are discussed. Whatever precautions are taken to use only the purest reagents and salts, and platinum crucibles, the ignited oxide is always found to contain some chromate. This may be shown by extracting with water. Hence, such methods lead to high results. It has been found that chromium can be quickly and accurately estimated volumetrically. The procedure is to add to an approximately neutral solution of a chromium salt an excess of sodium peroxide—about a gram—and boil for ten minutes to complete the oxidation to chromate and to decompose the unused peroxide. After acidification with either sulphuric or hydrochloric acid, excess of potassium iodide is added, and the liberated iodine titrated in the usual way.

*The Colorimetric Estimation of Lead in Cream of Tartar*, by R. L. ANDREW.

During 1921-22 all importations of cream of tartar to New Zealand were examined for lead, and the following method was found to give similar results and to be less cumbersome than the B.P. method. One cc. of 5 per cent. potassium cyanide solution, 1 cc. of ammonia solution, and 40 cc. of water are added to two grams of cream of tartar, and solution effected by warming and shaking. After cooling and filtering, any tint is matched in the standards by the addition of very dilute caramel. These standards are prepared in a similar way from 2 grams of lead, free from cream of tartar, with the addition of requisite amounts of lead nitrate solution containing 0.01 per cent. of lead. A few drops of 10 per cent. sodium sulphide solution are added, and the solutions are all made up to the mark and the amount of lead estimated by comparison. If a standard water solution of lead is used, a serious error is introduced, as the colour is only

about half the depth of that produced with a tartrate solution, and the effect of ferric and ferrous iron is investigated.

### THE SOCIETY OF GLASS TECHNOLOGY.

A meeting of the Society of Glass Technology was held in University College, Gower Street, W.C.1, on December 12.

The following papers were received and discussed:—

*An Apparatus for the Calibration of Burette Tubes*, by VERNEY STOTT, B.A., F.INST.P.

*Some Factors Affecting Efficiency in the Glass Trade*, by ERIC FARMER, M.A. (Industrial Fatigue Research Board).

*Specifications in the Glass Industry, with Special Reference to Soda-Lime Glasses for Containers*, by PROFESSOR W. E. S. TURNER, D.Sc.

### THE PHYSICAL SOCIETY OF LONDON.

A meeting of the Society was held on Friday, December 14, at the Imperial College of Science, South Kensington, S.W.

The following papers were read:—

*The Aerodynamic Resistance of Spheres Shot Upward to Measure the Wind*, by L. F. RICHARDSON, F.INST.P., F.R.MET.SOC.

*X-Ray Analysis of Zinc-Copper Alloys*, by E. A. OWEN, M.A., D.Sc., and G. D. PRESTON, B.A.

*Investigations of Piezo-Electric Effects with Dielectrics*, by K. R. BRAIN, B.Sc.

A Demonstration of "The Neon Tube Oscillograph" was given by H. St. G. Anson.

### THE OPTICAL SOCIETY.

A meeting was held at the Imperial College, South Kensington, on Thursday, Dec. 13. The following papers were presented and discussed:—

*The Primary and Secondary Constant Magnification Surfaces of Thin Lenses*, by T. SMITH, M.A., F.INST.P.

*A Suggested Standard Trial Case and Simplification in Ophthalmic Policy*, by W. SWAINE, B.Sc.

"An optical revolution counter" was exhibited and described by B. K. Johnson.

PROCEEDINGS OF THE GEOLOGICAL SOCIETY OF LONDON.

DECEMBER 5.

Prof. A. C. Seward, Sc.D.; F.R.S., President; and, afterwards, Dr. G. T. Prior, F.R.S., F.G.S., in the chair.

Dr. F. A. Bather exhibited, on behalf of Mr. A. S. Hirst, F.Z.S., specimens, microscope-slides, and lantern-slides of Arachnid Remains from the Rhynie Chert, and described their structure and affinities.

The following communications were read and discussed:—

*The Geology of the Northern Border of Dartmoor, between Whiddon Down and Butterdon Down*, by CHARLES WILLIAM OSMAN, M.INST.C.E., F.G.S.

*The Geology of Southern Guernsey*, by DONALD JOHN FARQUHARSON, M.Sc., F.G.S.

Rock-specimens and microscope-sections were exhibited by Mr. C. W. Osman, and microscope-sections were exhibited by Mr. D. J. Farquharson, in illustration of their respective papers.

A meeting of the Society was held on Wednesday, December 19.

Prof. W. J. Sollas, F.R.S., F.G.S., demonstrated the Method of Investigating Fossils by means of Serial Sections, and exhibited some of the results obtained.

Mr. John Walton, M.A., dealt with the Investigation of the Nature of Fossil Plants, illustrating his remarks by lantern-slides.

THE ROYAL INSTITUTION OF GREAT BRITAIN.

LECTURES BEFORE EASTER, 1924.

Friday Evening Discourses, addressed to members and their friends, at 9 p.m.:—

Jan. 18: PROF. HENRY E. ARMSTRONG, LL.D., F.R.S., M.R.I., *The Scientific Work of Prof. Sir James Dewar, LL.D., D.Sc., F.R.S., Fullerian Prof. of Chemistry (1877-1923)*.

Jan. 25: SIR ASTON WEBB, K.C.V.O., C.B., President of the Royal Academy, *The Future Development of London*.

Feb. 1: SIR WILLIAM BRAGG, K.B.E., D.Sc., F.R.S., M.R.I., Fullerian Prof. of Chemistry, *Recent Research on Crystalline Structure*.

Feb. 8: SIR ARTHUR EVANS, D.LITT., LL.D., F.R.S., F.S.A., Prof. of Prehistoric Archaeology, University of Oxford, *Recent Lights on the Minoan Art of Crete*.

Feb. 15: J. H. JEANS, LL.D., D.Sc., F.R.S., M.R.I., Secretary of the Royal Society, *The Origin of the Solar System*.

Feb. 22: G. ELLIOT SMITH, M.D., F.R.S., F.R.C.P., M.R.I., Prof. of Anatomy, University of London, *The Human Brain*.

March 7: WALTER ROSENHAIN, D.Sc., F.R.S., Superintendent of Metallurgy Department, National Physical Laboratory, *The Inner Structure of Alloys*.

March 14: J. W. MACKAIL, LL.D., F.B.A., Hon. Fellow of Balliol College, Oxford, *"The Pilgrim's Progress"*.

March 21: SIR FREDERICK KEEBLE, C.B.E., Sc.D., F.R.S., Sheradian Prof. of Botany and Fellow of Magdalen College, Oxford, *The Plant Commonwealth and its Government*.

March 28: HUGH MACLEAN, M.D., D.Sc., Prof. of Medicine, University of London, *Insulin*.

April 4: SIR ERNEST RUTHERFORD, LL.D., D.Sc., F.R.S., M.R.I., Prof. of Natural Philosophy and Cavendish Prof. of Experimental Physics, University of Cambridge, *The Nucleus of the Atom*.

April 11: JOCELYN THORPE, C.B.E., D.Sc., F.R.S., Prof. of Organic Chemistry, Imperial College of Science and Technology, *Colours, Stains and Dyes*.

JUVENILE CHRISTMAS LECTURES—THREE O'CLOCK, AFTERNOON.

*Concerning the Nature of Things*, by SIR WILLIAM BRAGG, K.B.E., D.Sc., F.R.S., M.R.I., Fullerian Prof. of Chemistry.—

Ninety-Eighth Course, adapted to a Juvenile Auditory (Illustrated):—

(I.) *The Atoms of which Things are Made*; (II.) *The Nature of Gases*; (III.) *The Nature of Liquids*; (IV.) *The Nature of Crystals: The Diamond*; (V.) *The Nature of Crystals: Ice and Snow*; (VI) *The Nature of Crystals: Metals*.

(I.) Thursday, Dec. 27; (II.) Saturday, Dec. 29; (III.) Tuesday, Jan. 1; (IV.) Thursday, Jan. 3; (V.) Saturday, Jan. 5; (VI.) Tuesday, Jan. 8.

#### GENERAL COURSES OF LECTURES BEFORE EASTER, 1924.

Tuesdays and Thursdays at 5.15 p.m.; Saturdays at 3 p.m.:—

Tuesdays, Jan. 15, 22: *Drug Addictions*, by WALTER E. DIXON, M.D., F.R.S., Prof. of Pharmacology, King's College, London.

Tuesdays, Jan. 29, Feb. 5: *What is Heredity?* by ARTHUR DENDY, D.Sc., F.R.S., Prof. of Zoology, University of London (King's College).

Tuesdays, Feb. 12, 19, 26, March 4: *The Respiratory Pigments in Animal Life and Their Significance*, by JOSEPH BANCROFT, C.B.E., F.R.S., Fellow of King's College, Fullerian Prof. of Physiology.

Tuesdays, March 11, 18: *Recent Investigation Concerning the Safety of Railway Bridges*, by MAJOR C. E. INGLIS, O.B.E., M.A., A.M.INST.C.E., Prof. of Engineering, University of Cambridge.

Tuesdays, March 25, April 1, 8: *Ballads*, by GEORGE GORDON, Merton Prof. of English Literature, University of Oxford.

Thursdays, Jan. 17, 24, 31: *Straws from Cumberland Market*, by WALTER SICKERT.

Thursdays, Feb. 7, 14, 21, 28: *The Crystalline Structure of Organic Substances*, by SIR WILLIAM BRAGG, K.B.E., D.Sc., F.R.S., M.R.I., Fullerian Prof. of Chemistry.

Thursdays, March 6, 13: I., *Modes of Volcanic Action*; II., *Types of Volcanic Structures*, by JOHN S. FLETT, D.Sc., LL.D., F.R.S., Director of H.M. Geological Survey and Museum of Practical Geology.

Thursdays, March 20, 27: *Evolution Today*, by D. S. M. WATSON, M.Sc., Jodrell Prof. of Zoology and Comparative Anatomy, University of London.

Thursdays, April 3, 10: *Scientific Research on Sea Fisheries*, by E. J. ALLEN, D.Sc., F.R.S., Secretary of the Marine Biological Association and Director of the Plymouth Laboratory.

Saturdays, Jan. 19, 26, Feb. 2: I., *The Mechanical Reproduction of Music*, by REGINALD REYNOLDS, A.G.S.M. (with musical illustrations); II., *The Couperin Dynasty*; III., *The Influence upon Composition of Improvements in Musical Instruments*, by WILLIAM WALLACE (with musical illustrations).

Saturdays, Feb. 9, 16: *The Last Years of the Scottish Parliament*, by ROBERT S. RAIT, C.B.E., LL.D., Historiographer Royal for Scotland.

Saturdays, Feb. 23, March 1: I., *Imaginative Prose*; II., *Character in Fiction*, by WALTER DE LA MARE.

Saturdays, March 8, 15, 22, 29: *Properties of Gases in High and Low Vacua*, by SIR ERNEST RUTHERFORD, LL.D., D.Sc., F.R.S., M.R.I., Prof. of Natural Philosophy, R.I., and Cavendish Prof. of Experimental Physics, University of Cambridge.

Saturdays, April 5, 12: I., *Aristotle as a Biologist*; II., *Leonardo da Vinci as a Man of Science*, by CHARLES SINGER, D.LITT., M.D., F.R.C.P., Lecturer on the History of Medicine, University of London, University College.

#### THE FARADAY SOCIETY.

*First (Experimental) Report to the Atmospheric Corrosion Research Committee (of the British Non-Ferrous Metals Research Association)*, by W. H. J. VERNON, B.Sc., read on Monday, December 17.

The research has proceeded mainly along two lines. "Field Tests" have been carried out with relatively large specimens exposed to representative atmospheres, with the primary objects of (a) comparing the effects of these atmospheres upon typical metals and alloys, and (b) correlating the behaviour, among themselves, of as wide a range of materials as possible. Laboratory experiments, on the other hand, were conducted upon relatively small specimens, with the object of obtaining information concerning the mechanism of atmospheric corrosion.

The work was divided into two parts, devoted respectively to these main branches of the work. Although much the greater amount of time has been expended in the former direction, actually the results so obtained have contributed largely to the object envisaged by the latter; for this reason the distinction between the two parts has not been retained in summarising the re-

sults. It should be stated that in consequence of the comparatively early stage which it represents, the present report is occupied, in the main, only with the phenomenon of *tarnishing*, as distinct from corrosion in the ordinary sense.

The types of atmosphere investigated included (1) an indoor atmosphere maintained continuously in the unsaturated condition with respect to water vapour. (2) An indoor atmosphere of variable (but relatively high) humidity, occasionally reaching saturation. (3) An ordinary domestic kitchen. (4) Open-air exposure (at South Kensington).

The methods of examining and estimating tarnish films were: (1) Visual (supplemented, as occasion required, by the microscope). (2) Optical. After suitable preparation, the *reflectivities* of metal surfaces have been determined, (a) in the freshly-cleaned condition, (b) during the course of exposure. The loss of reflectivity affords a very sensitive means of estimating the changes taking place at the surface, applicable more particularly to the earliest stages of tarnishing. (3) Gravimetric. Accurate determinations have been made of the *increase in weight* of the test-plates, at intervals during the whole period of indoor exposure, and also in the very early stages of open-air exposure. In the case of indoor conditions, interesting relationships have been found to obtain between weight-increment and period of exposure.

The significance of the shape of the curve obtained by plotting weight-increment against time was discussed in relation to the function of the corrosion product or "scale," and the principle involved appears to be of much importance. Three types of curve have been distinguished:

(1) A *parabola* whose axis coincides with the *time-axis* of co-ordinates. Weight-increment is thus proportional to the square root of time, *i.e.*, the rate of attack is retarded as the period of exposure increases. The *scale* forms a continuous envelope, the rate of diffusion of the corroding atmosphere through which regulates the attack upon the underlying metal. *Example*: Copper, within a wide range of humidity conditions.

(2) A *straight line* passing through the origin. Weight-increment is directly proportional to time, *i.e.*, the rate of attack remains constant as the period of exposure increases. The *scale* is completely permeable, allowing free access of atmosphere to

the metal, and itself playing a neutral part. *Example*: Zinc, in an unsaturated atmosphere.

(3) A *parabola* whose axis coincides with the *weight-axis* of co-ordinates. Weight-increment is proportional to the square of time, *i.e.*, the rate of attack is accelerated as the period of exposure increases. The *scale* is discontinuous, and accelerates the attack upon the remaining metal in proportion to the amount which is already present. *Example*: Iron in an atmosphere of relatively high humidity, intermittently reaching saturation.

Whilst no appreciable difference has usually been observed by ordinary visual examination between the behaviour of emiered and brightly-polished surfaces respectively, the optical and gravimetric methods have shown under certain conditions a greater degree of tarnishing on the rougher surface. Under "inside" conditions the maximum differences have been observed in the atmosphere of low relative humidity. In the more humid atmosphere, "dull" and "bright" surfaces have given practically identical results (both as regards weight-increment and percentage loss of reflectivity).

In the atmosphere of the kitchen, anomalous results have been observed, particularly with silver and silver-copper alloys, fine silver then showing, by *all* methods of examination, a greater degree of tarnish on the *polished* surface; on the other hand, in the case of the standard alloy, the normal result obtains but to an exceptional and excessive degree, the brightly-polished surface then being relatively immune from attack.

In all instances investigated the difference in behaviour between materials having the maximum degree of hardness and of softness respectively has been exceedingly small—always below the limits of visual detection, and frequently incapable of estimation even by the optical method. Wherever an appreciable difference has been recorded, however, the harder material has always been found to have undergone the greater amount of change; the difference is more readily detected with dull-polished (emiered) than with brightly-polished specimens.

A considerably greater degree of tarnishing obtains during the winter than during the summer months, even in an indoor atmosphere in which no combustion processes are carried on, the difference being due, pre-

sumably, to the greater pollution of the atmosphere during the former period. Moreover, the incidence of cold spells of weather is also accompanied by an increase in the rate of tarnishing, due doubtless to the same cause. It is important to note, however, that these remarks refer to initially-clean surfaces exposed during the periods concerned. With copper, and copper-rich alloys, the rate of tarnishing is controlled (within a wide range of atmospheric conditions) by the nature of the tarnish film which is initially formed.

#### THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

Paper read at the Royal Society of Arts, on December 11:

*The Modern Rotary Drilling System*, by L. R. McCOLLUM.

The percussion, or cable tool method of drilling, which Col. Drake first used in 1859, has changed but little in principle.

It has proved a reliable method for drilling in most fields, and its use has been widespread throughout the United States, and in many foreign fields.

Later, exploitation work in the Gulf Coast regions of Texas and Louisiana encountered unconsolidated, soft, and caving formations, which gave the cable tools a bad time. To combat these conditions the Rotary system was invented, or rather developed, upon the Fauck system, which had been in use in Europe since 1845.

By this method a rigid stem of pipe rotates a fish tail—or other type of bit—at the bottom of the hole, being assisted by the action of clay mud in the fluid state, pumped under hydraulic pressure, through the drill pipe. The circulating mud also removes the cuttings from the hole.

So great were its virtues of speed and economy that modifications and improvements were soon added which enabled it to penetrate thick strata of extremely hard rock at great depths. This capacity has now been probed beyond the questioning of intelligent operators.

The extreme speed attained with this type of equipment, and the few strings of casing necessary, are its chief assets.

One of the objections which is raised against the Rotary system by operators unfamiliar with its working, is that there is the danger of mudding off unknown oil sands, but it was pointed out that this risk was very small and could be overcome.

The author went on to describe the principle and accessories of the system, and dealt with such matters as mud storage, power, pumps, the actual operation and speed attainments. The advantages of the method were well brought out.

The Library of the Chemical Society will be closed for the Christmas holidays from Monday, December 24, to Thursday, December 27, inclusive.

#### NOTICES OF BOOKS.

*Valence and the Structure of Atoms and Molecules*, by PROFESSOR G. N. LEWIS. Pp. 172. 1923. The Chemical Catalog Company, 19, East 24th Street, New York, U.S.A. (American Chemical Society Monograph Series). Price \$3.00.

Prof. G. N. Lewis, the pioneer in the structure of atoms and molecules as based upon electrons arranged at the corners of cubes, has written a monograph of considerable value. Of particular historical interest in this connection is a reproduction of his original sketches of atoms, as made in 1902.

This book is in the nature of a survey, in which some of the present-day theories of the atom are clearly expounded. It seems a little extraordinary that so much space should be given up to the Bohr atom, seeing that Prof. Lewis was the originator of a theory quite as interesting and valuable; but this is no doubt done in a spirit of fairness, though one might have expected the pioneer of the octet theory to have given his whole attention to its elucidation and expansion as developed by other workers.

Referring to the attempt to co-ordinate the static theory with the dynamic, this, as far as expounded by Prof. Lewis, cannot be said to be at all successful, but this comment is not in the nature of an adverse criticism, since one is compelled to make the most of co-ordination ideas in books of this type.

Many of the more or less usual introductory statements appear, but the implication that Helmholtz, in 1881, was the first to make important observations that electricity was atomic in character is not historically true. Wilhelm Weber, in 1871, introduced in his theoretical work the idea of particles of positive and negative electricity, and went so far as to postulate that the + particle described an orbit round the - particle, thus indicating the "Amperian

molecular current," to quote his words. In 1874, G. Johnstone Stoney, at Belfast, read a paper (printed later), in which the elementary electrical charge was clearly enunciated, and an attempt was made to evaluate its magnitude which approximated to the truth; and, moreover, Prof. Stoney, in 1891, designated this charge by the name *electron*. The later work of H. A. Lorentz is not mentioned. The reviewer does not presuppose that Prof. Lewis was unaware of these matters, but the omissions are, nevertheless, apparent: an oversight, no doubt.

On page 33, the Lewis and Kossel models are depicted side by side, the former being cubic and the latter an arrangement of the electrons in one plane, the outer number in these examples being 8, the octets being completed ones. On the same page Lewis says:—"In this connection I emphasised the peculiarity of hydrogen which, by giving off an electron, can become the simplest of positive ions, consisting solely of an atomic nucleus, while by taking on one electron it can complete the group of two, characteristic of the helium atom. This process seemed so nearly like the taking on of one electron by fluorine or by chlorine to form F<sup>-</sup> or Cl<sup>-</sup>, with structures corresponding to neon and argon, that I felt justified in regarding hydrogen as belonging, in this respect at least, to the halogens; and therefore predicted that metallic hydrides would prove to have the character of salts, consisting of metal ion and hydride ion, and further that electrolysis of a hydride should produce hydrogen at the anode. This prediction has been entirely verified in the work of Bardwell (1922), who succeeded in electrolyzing a melt containing calcium hydride, and obtaining hydrogen at the anode in amount corresponding to Faraday's law."

In Chapter III, the spectral lines are well illustrated and the "physicist's view of the atom" given. The Lyman, Balmer, Paschen and Brackett series formulæ are stated on page 38, together with diagrams illustrating the principal lines and the "basic frequencies of hydrogen." The quantum theory is dealt with at some length, and the energy levels in the H atom diagrammatically given on p. 43. X-ray spectra, ionisation, and resonance potentials are treated briefly.

On page 50 the following appears:—"It was predicted from the classical electromagnetic theory that any accelerated charge would emit radiant energy, but the electron

in one of the stable orbits of the Bohr theory is subject to constant acceleration toward the centre of the atom, and yet it is supposed to emit no radiation. However, such emission of energy from an accelerated charge does not seem to be an entirely inevitable consequence, even of classical theory, and for this reason we may turn our attention to a still more elementary way in which I have attempted to show (1917) the divergence between the properties of the Bohr atom and the properties that would formerly have been assumed for a system containing an electron in motion." The argument that follows here is interesting and should be studied in the original.

On page 58 Lewis records that "in a recent investigation of extraordinary interest, Stern and Gerlach (1921) have succeeded in studying in a most direct manner the magnetic properties of the silver atom, which, like the hydrogen atom, we suppose to have one electron in its outer shell. They find that its behaviour is similar to that which would be predicted for the hydrogen atom by the Bohr theory." Further, on page 66, we find the following:—"In the meantime it must be admitted that the problem is by no means completely solved. Both Bohr and Bury assume that the last fragmentary period of the Mendeléeff table is a period of thirty-two elements; but I have pointed out in a previous chapter that the properties of thorium and uranium indicate a far less resemblance to the preceding period of thirty-two than to the next preceding period of eighteen." We may remark here that Loring's wedge table accords with Lewis in this respect.

Of particular interest, the part from Chapter V. onwards may be noted. Here we find discussions of the union of atoms, the chemical bond, pairing of electrons, double and triple bond, limitation of multiple bonds, exceptions to the rule of eight, valence and co-ordination number, quadrivalence of nitrogen, valencies higher than four, valence and condensed systems, compounds of elements with small kernels, elements in positive and negative states, electromers, &c.

Finally, we may quote from page 142, as follows:—"We are inclined to think of substances as possessing acid or basic properties, without having a particular solvent in mind. It seems to me that with complete generality we may say that a basic substance is one which has a lone pair of electrons which may be used to complete

the stable group of another atom, and that an acid substance is one which can employ a lone pair from another molecule in completing the stable group of one of its own atoms. In other words, the basic substance furnishes a pair of electrons for a chemical bond; the acid substance accepts such a pair." Prof. Lewis (page 148) regards the pairing of electrons "as the most fundamental phenomenon in all chemistry."

A list of references is given at the conclusion of the book. The book is indexed (but this might be slightly improved—a statement which applies to most books), and the printing and binding is, of course, up to the best standard.

*Kolloide in der Technik*, von DR. R. E. LIESEGANG. Pp. 157. Dresden & Leipzig. Verlag von Theodor Steinkopff. 1923. Price 3s. 6d.

The importance of a thorough knowledge of the principal phenomena exhibited by substances in the colloidal condition is now becoming recognised by technologists.

Prof. Liesegang has presented, in this volume, a very interesting account of the application of these principles to various technical and industrial processes. He gives a very good resumé of the recent theoretical and practical advances that have been made.

From a description of the behaviour of bodies in the colloidal state as exemplified by gelatin and similar bodies, and the protective colloids, he passes to their connection with such processes as that of tanning and those, for instance, of the textile industries.

Soaps, oils, resins, rubber, the metals, ceramics and foodstuffs are all discussed from the point of view of colloids.

The final chapter on Photography has been very ably written, and contains an excellent account of the latest work and theories in all the processes encountered in this field.

The references to British and American workers and their researches are surprisingly good when it is remembered that German scientists encounter great difficulties in obtaining information concerning scientific work carried on outside their country.

*Uses of Waste Materials*, by PROF. ARTURO BRUTTINI. Pp. XX. + 367. 1923. Messrs. P. S. King & Son, Ltd., Orchard House, 2 & 4, Great Smith Street, Westminster. 12s. net.

The author has collected much useful in-

formation on the utilisation of waste materials during the years 1914-22, for making human and animal foods, and for agricultural fertilisers.

For many of these products, it may be noted that no essentially new process was involved, but instances are given where new and often ingenious methods were adopted.

Attention is drawn to the importance of profiting by these experiences. Processes of proved economic value should be retained and developed in the future. It will be realised that many of the substitutes manufactured during the war in the belligerent nations were of no permanent importance, since they were introduced to meet exceptional and temporary needs.

In Part I. the author gives the legislative measures adopted for the utilisation of waste products as foods, etc.

Part II. contains a detailed account of the collection and treatment of various types of waste. The limits to which Germany was driven by the war in her efforts to provide substitutes for almost every item of food are fully realised by a perusal of Prof. Bruttini's compilation. Yeast, blood, potatoes, straw, meal, etc., were all used in eking out flour in bread-making. Various plant products were employed for making something to resemble coffee, and a valuable list of wild plants fit for human consumption is given. The substitutes for meat and table oils in the Central Empires were naturally far removed from the articles they were intended to replace.

Great ingenuity was displayed by agriculturists in all countries during the period under review, in opening up new sources of fodder. Matter of more permanent value is, however, to be found in the section on fertilisers. Residues from many industries could well be utilised as fertilisers to a far greater extent than is at present realised. Undoubtedly a more scientific and intensive use of waste can be achieved, involving a saving of much wealth at present lost. This monograph very clearly shows the lines on which the problem should be attacked.

A number of misprints have crept into this excellent work. These should be corrected in future editions, which may be confidently expected.

*Industrial Filtration*, by ARTHUR WRIGHT, M.E. Pp. X. + 336. Vol. I., 1923. The Chemical Catalog Co. Inc., 19, East 24th Street, New York, U.S.A. \$5.00.

There are so few books on specific indus-

trial processes, and it is noteworthy that this is the first of a new series, each volume of which is to be devoted to one particular process. Among those to follow are volumes on *Heat Transfer and Evaporation*; *Theory and Practice of Evaporation*; and *Fractional Distillation*.

The present volume is divided into three parts. In the first part, the author discusses such matters as clarification, cake building, washing, drying, and discharging; filter media, and auxiliary equipment. This section is entitled *Theory of Filtration*, which is somewhat misleading to an English reader (this is an American publication).

Part two, the *Mechanics of Filtration*, gives a useful account of certain types of filters and presses now used, although there is no mention of centrifugal apparatus.

Part three is concerned with the applications of the various types of plants described, and the general works practice.

The author's aim has been to emphasise the importance of the fundamental principles, and to discuss the merits of certain types of American machines. This latter has unfortunately given the book somewhat the aspect of a commercial catalogue.

The book will be helpful to many technical chemists who have filtration problems to contend with.

The Department of Overseas Trade has published (through H.M. Stationery Office) a *Report on the Economic Conditions in South Africa*, by MR. W. G. WICKHAM, H.M. Senior Trade Commissioner in South Africa; July, 1923, price 1s. 6d. net.

Among industrial raw materials, soda ash, caustic soda and potash show considerably increased importation at lower price levels. On the other hand, in spite of the lower price, we find actually a reduction in the quantity imported of nitrates, glycerine, sulphur, and cyanides. The dislocation in gold mining and cessation of diamond mining are no doubt responsible directly and indirectly by reducing the demand for the locally manufactured explosives.

Paraffin wax shows an importation doubled in quantity, but at a much reduced price. Vegetable and mineral oils are also lower in price, but demand has not fully responded to this stimulus.

#### BOOKS RECEIVED.

*The Life of Sir William Crookes*, M., F.R.S., by E. E. FOURNIER, D. ALBE., D.Sc., F. INST. P., with a foreword by SIR

OLIVER LODGE. Pp. XVII. + 409. 1923. Messrs. T. Fisher Unwin, Ltd., Adelphi Terrace, W.C.2. 25s. net.

*The British Journal Photographic Almanac for 1924*, Edited by GEORGE E. BROWN, F.I.C. Pp. 812. Henry Greenwood & Co., 24, Wellington Street, Strand, W.C.2. Paper, 2s. net.; cloth, 3s. net.

*Molekulargrößen von Elektrolyten*, von DR. PHIL. ET CHEM. PAUL WALDEN. Pp. XI. + 350. 1923. Verlag von Theodor Steinkopff, Residenzstr. 12b, Dresden und Leipzig. 11s. 6d.

*The Principal of Relativity*, by ALBERT EINSTEIN, H. A. LORENTZ, H. MINKOWSKI, A. SOMMERFELD, H. WCYL; Translated by G. B. JEFFERY, D.Sc., and W. PERRETT. Ph.D. Pp. VIII. + 216. 1923. Messrs. Methuen & Co., Ltd., 36, Essex St., W.C.2. 12s. 6d. net.



This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

#### Latest Patent Applications.

30305—Bredig, G.—Production of cyanide compounds. Dec. 1.

#### Abstract Published this Week.

205288—Nitrogen oxides.—Goodwin, C. J., of 7, Idol Lane, London.

In the production of nitrogen oxides by exploding a mixture of combustible gas and air of oxygen in a bomb or engine, the combustible gas, such as coke oven gas, coal gas, water-gas, or producer gas, is treated to increase its nett calorific value by removing some or all of its free hydrogen.

The invention is described with particular reference to coke oven gas, and the hydrogen alone, or the hydrogen and carbonic acid are removed. The removal of the hydrogen may be effected in any suitable manner, either physical, such as liquefaction or low-temperature separation, or chemical, as by adding carbon monoxide and using the mixture to synthesise methyl or ethyl alcohol under pressure by catalytic or other means, the remaining gas in this last case being mainly methane. When the hydrogen is removed as such it may be converted into ammonia by the known synthesis.

Messrs. Rayner & Co. will obtain printed copies of the published specifications and abstract only, and forward on post free for the price of 1s. 6d. each.

Mr. Edward C. Davies, M.Sc., a distinguished student of Prof. Robert M. Wild at Manchester University, has been appointed as Assistant Lecturer in Chemistry at the Natal Technical College, Durban, S. Africa.



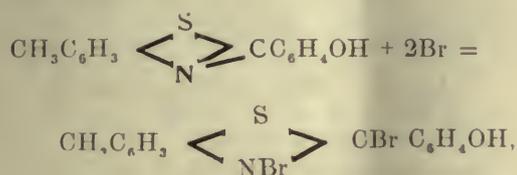
# THE CHEMICAL NEWS,

VOL. CXXVII. No. 3324.

## 4' HYDROXY 1 PHENYL 5 METHYL-BENZOTHAZOLE AND ITS BROMINATION.

By R. F. HUNTER.

If the considerations which have already been put forward by the author as to the structure of the dibromination products of dehydrothiitoluidin and its derivatives are correct, then, since the phenolic derivative of this benzothiazole contains the usual thiazole ring containing the double bonded nitrogen and carbon atoms, the 4' hydroxy 1 phenyl 5 methylbenzothiazole should add bromine according to the equation:—



when dissolved in glacial acetic acid. A point, however, arises, and that is whether the presence of the hydroxyl group in the benzene part of the molecule might not produce a tendency towards substitution in addition to the bromine addition to the thiazole ring. If such a tendency does exist, then clearly we should expect that a precipitate would be formed when bromine is added to the aqueous solution of the phenol in a manner analogous to the precipitation of tribromophenol from aqueous solutions by means of bromine water. The 4' hydroxy 1 phenyl 5 methyl benzothiazole was therefore prepared and examined by the method given in the experimental portion of this paper. Addition of bromine to a solution of the compound in glacial acetic acid produced the expected precipitate of the usual type. Addition of bromine water to an aqueous solution of the compound apparently had no action. This evidence cannot be considered of very great importance, since the solubility of the phenol of dehydrothiitoluidin is very low. On the other hand addition of bromine water to an alcoholic solution of the compound produced a grey flocculent precipitate, which quite possibly was unchanged, the base

settling out owing to the diminished solubility in the solvent. The quantity was, of course, too small for investigation.

### EXPERIMENTAL.

1.5 gm. of pure dehydrothiitoluidin from alcohol is dissolved in the minimum of fairly strong sulphuric acid in a 250 cc. flask. The solution is cooled under the tap. 0.5 gm. of sodium nitrite dissolved in 3 ccs. of water is then added to the cooled solution. The resulting solution is then heated on a boiling water bath till the evolution of nitrogen ceases, a red brown tarry solid remaining, which floats on the surface of a similarly coloured liquid. It was wrongly thought that the compound might be volatile in steam, so that the flask and its contents were therefore steam distilled for three hours, and the distillate searched for a substance with phenolic properties in vain. The solid remained quite unaffected in the flask during the distillation. The acid present was neutralised with strong caustic soda solution. Further addition caused sudden and nearly complete solution as a deep brown liquid. This was filtered from a small black residue to a deep brown clear liquid, to which hydrochloric acid was added drop by drop, with the immediate formation of a yellow brown precipitate. The addition of acid was continued until nothing more was precipitated. The liquid was then filtered, and the precipitate washed and dried. The phenol remained on the filter paper as a pale brown solid.

A portion was dissolved in glacial acetic acid, and bromine was added drop by drop from a burette. A brown precipitate formed at once. The precipitation was completed by drowning with cold water, after allowing the beaker containing the bromination product and excess bromine to stand for a few minutes.

A small amount of the phenol was dissolved as completely as possible in hot water, the solution filtered, and bromine water added to the filtrate. There was no precipitate.

A small amount of the substance was dissolved in alcohol in the same way, and bromine water was added. A grey flocculent precipitate resulted.

*The Imperial College of Science and  
Technology, S.W.7.*

September, 1923.

## "DRY-ROT" DISEASE OF TIMBER.

By E. H. ELLIS.

Amongst other non-chemical problems upon which industrial chemists are required to give advice, the control of "dry-rot" of timber is one of annoying persistence.

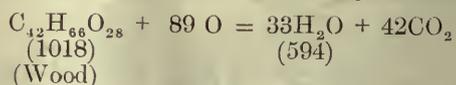
"Dry-rot" is caused principally by the fungus *Merulius lacrymans*. It is a disease of civilisation. Indeed, quite apart from the fact that the actual dry-rot fungus grows only upon worked wood and is rarely, if ever found on living trees, the term "dry-rot" has been restricted by architects and timber-merchants to the rot of worked wood; many fungus diseases produced in the standing timber being known collectively as "wet-rot."

Infection of wood often occurs during storage in a timber yard. The spores of dry-rot, although capable of remaining viable for a period of years, apparently infect sound wood with difficulty. Hence infection is rarely caused by the spores, being commonly due to the spread of the mycelium. Also, during periods of drought, the protoplasmic contents of the mycelium become agglomerated, the cell-walls break up into small resting bodies (oidia), which are easily scattered, and which germinate readily, causing re-infection.

In spite of its name, the "dry-rot" fungus, like all fungi, must have moisture to enable it to grow; the term "dry-rot" referring rather to the condition of wood attacked by the fungus than to the fungus itself.

When a piece of constructional timber is attacked by dry-rot, two distinct types of growth may be seen. The first consists of a fine network actually inside the wood, which supplies the proteins essential to fungus growth. The threads composing the network secrete various enzymes as hadromase, cytase and emulsin, by which the coniferin (constructional timber is usually coniferous), and cellulose of the cell-walls are dissolved, and a residue of lignin, tannin and calcium oxalate is left behind. So long as sufficient moisture is present the wood retains its original volume, but with the gradual withdrawal of water numerous right-angled cracks appear. Under certain conditions of moisture a skin-like growth or balled pads of the fungus may invest a timber balk. Sometimes, principally through either a lack of food material or moisture, the filaments of the fungus grow together,

forming white cords, which later become a slaty-grey colour and may become about a quarter of an inch thick. The cords have a characteristic structure, and examination with a microscope reveals three kinds of threads that can be distinguished according to their size and the thickness of their cell-walls. There are thin-walled threads of normal width; long and wide, water-conducting-threads; and fibrous threads, whose thickened walls serve for mechanical support. The whole fungus may glisten with drops of extruded water, possibly for ultimate conduction to the point of attack upon the drier parts of the wood. These tear-drops are not conducted from the source of water-supply, but are formed by the respiration of the fungus. The principle involved is mainly one of oxidation of the host wood. Oxygen from the air is essential for respiration. Adopting an empirical formula for wood, the dry-rot fungus has been shown to be able to produce water to about half the weight of the original wood.



Thus the dry-rot fungus can actually produce the moisture necessary for its own existence. The formation of oidia, or the variously coloured fruit bodies, is more or less an indication of local failure of water supply or food material. The superficial growth can also be related to local shortage of water supply, and by means of it the fungus can spread over such unpromising material as brickwork and tiles, and can penetrate mortar and thus attack distant wood.

"Dry-rot" has been the reputed cause of various human diseases, but this is impossible, as blood heat is fatal to the fungus.

In questions of control a distinction must be drawn between prevention of infection, and dealing with existing infection. In the first case, contact with infectious material must be guarded against, only well-seasoned wood should be selected, and sawn wood should be stored in the dry and be well ventilated. Buildings in which the timber is afterwards used should also be well ventilated.

Timber can be treated with antiseptics, but this method is very costly, as for perfect success the wood must be impregnated. Copper sulphate, iron sulphate, zinc chloride and mercuric chloride have been recom-

mended, but are impracticable. Sodium fluoride, boric acid, and above all, magnesium silicofluoride, have been found to be the best inorganic preservatives. Amongst organic preservatives creosote and tar, but their colour and smell restrict their use.

Dinitrophenates and dinitroresates of potassium and sodium are effective, particularly the sodium salt of dinitrophenol, which, however, is decomposed by light, and, being explosive, must be mixed with an inert substance. Kiln drying of wood has also been recommended.

When dealing with an existing attack of "dry-rot," infected wood must be removed, surrounding woodwork examined, and exposed surfaces disinfected. Walls and woodwork may be washed with formalin, and finally coated with an antiseptic. Care should be taken to obviate future damp.

[An excellent critical account of "dry-rot" and also of many other fungus diseases of timber may be found in the "Handbook of the Larger British Fungi," by Mr. J. Ramsbottom, the well-known authority on these matters, recently published by the British Museum (Natural History).]

### WHAT IS A CHEMICAL?\*

By J. N. TAYLOR, M.S.<sup>1</sup>

There has recently come about a most interesting discussion regarding the definition of a synthetic organic chemical. According to *Chemical Age* (New York) for April, 1923, the Board of Governors of the Synthetic Organic Chemical Manufacturers' Association has adopted the following definition: "Synthetic Organic Chemical—An organic chemical which has been produced by a controlled process involving change in chemical identity." A "chemical" is defined as "a material containing a preponderating proportion of an individual substance of definite elementary composition." Attention was called to these definitions in an editorial appearing in *Chemistry and Industry* for May 18, 1923, and further

reference was made to the definition of "synthetic organic chemical" by Mr. E. Parry in giving testimony at the hearing (June 15, 1923), on "Formaldehyde," under the Safeguarding of Industries Act (England), as to whether or not formaldehyde is a *synthetic organic chemical*. He observed<sup>2</sup> "that the difficulties of definition had become so great in the United States that only this month the Synthetic Organic Chemical Manufacturers' Association of the United States had attempted to define a synthetic organic chemical, but the definition arrived at was meaningless."

The subject of chemical nomenclature is one of general interest, engaging the attention of educators in the science as well as the various chemical societies and other associations having for their object the advancement of science. Some time ago the present writer took occasion to direct attention to the desirability of greater uniformity in chemical terminology,<sup>3</sup> especially in our schools and colleges. A number of welcome and helpful criticisms of the paper were received pointing out that the English language is a growing one, that it is yet in process of evolution, and that growth and change in our language demand simpler and more concise forms for conveying chemical ideas. This is indeed true. In any live, growing language, words change in meaning in the course of time. Couch, in his admirable series of articles now appearing in the *American Journal of Pharmacy*, entitled "The Evolution of Chemical Terminology," traces this very interesting development of our science. Divergences in the connotation of a word or term, recognisably depend in great measure upon the aspect which the word or term assumes. Such terms as "chemical" and "synthetic organic chemical," for example, might each convey different meanings from the point of view of a manufacturer, a dealer, a teacher, or an analyst, or when viewed from the standpoint of the tariff or the census, or when thought of as entering into interstate commerce.

<sup>2</sup> "Chemistry and Industry." (*Jour. Soc. Chem. Ind.*) Vol. XLII., No. 26, p. 643.

<sup>3</sup> Taylor, J. Norman: "Chemical Nomenclature and Pronunciation," *School Science and Mathematics*, Chicago, Vol. XX., No. 9 (1920). Reprinted in *Jour. American Pharm. Assoc.*, Philadelphia, Vol. X., 10-11 (1921), and in *Chem. News*, London, Vol. CXXII., 7 (1921).

\* Reprinted from "The American Journal of Pharmacy," Philadelphia., Pa., October, 1923.

<sup>1</sup> Instructor in Chemistry at the Washington Preparatory School and at George Washington University.

Certain words, when used in a legal sense, are specifically defined, and the extent to which an adjective may partake of the attributes of the noun are, therefore, limited by definition. Certain Acts of Congress specify for the purposes of the Acts the limits in meanings of certain words. For example, the Food and Drugs Act, June 30, 1906, defines the term "drug" as used in the Act as "all medicines and preparations recognised in the U.S. Pharmacopœa or National Formulary for internal or external use, and any substance or mixture of substances intended to be used for the cure, mitigation or prevention of disease of either man or other animal." The noun "drug" and terms derived from it are, therefore, circumscribed in meaning when employed under the provisions of the Act. As another example may be mentioned the word "insecticide." The Insecticide Act of 1910 defines "insecticide" as follows:—"The term 'insecticide' as used in this Act shall include any substance or mixture of substances intended to be used for preventing, destroying, repelling or mitigating any insects which may infest vegetation, man or any animals or households, or be present in any environment whatsoever." Naturally, the adjective "insecticidal" is limited in meaning for the purpose of the Insecticide Act, because of the meaning given the word "insecticide" by the framers of the Act. On the other hand, the popular meaning of words such as are noted above may extend beyond the limitations set down for them *ex cathedra*.

As an adjective, there appears to exist little, if any, confusion regarding the use of the term "chemical." We are accustomed to speak of "chemical reactions," "chemical compounds," "chemical products," etc., and, through custom and usage, their meanings carry no ambiguity. To what extent, however, may the popular concept of the meaning of the adjective be applied to the noun? When an attempt is made to distinguish between "chemical" and "chemical compound," between "chemical" and "drug," or between a chemical and the result of a chemical process, there appears to be a misunderstanding as to just what is conveyed when the word, "chemical," is employed as a noun.

It would seem apropos, therefore, in view of the present discussion of the meaning of the noun "chemical," to reaffirm the province of chemistry, hoping thereby

to establish a position from which we can survey this question in the light of both theory and practice.

Chemistry investigates the composition and properties of substances and the changes which they undergo. It deals with the energy changes within and between or among molecules and atoms of substances. Hence, in its application, it includes all material things which are the result of energy transformations. To the chemist, therefore—and who should be better qualified to speak on chemical topics than the chemist?—all substances which enter into and result from such energy transformations are chemicals.

There is nothing original in this statement, however. Munroe,<sup>4</sup> as long ago as 1905, in his monograph, "Chemicals and Allied Products," in discussing the classification of materials coming within the scope of the investigation for the Bureau of the Census, declared that, "*in the strictest technical sense every material thing is a chemical.*"

Obviously, until some such fundamental definition of a chemical is agreed upon and the start is made from this base, the efforts to obtain divisional definitions that will be generally accepted will be unavailing. With this in mind the foregoing definition is presented for consideration.

## THE SITUATION IN THE COAL INDUSTRY.

### ATTITUDE OF THE COLLIERY OWNERS.

In view of the unauthorised and contradictory statements that have appeared in the press with reference to the meeting on December 13 of the sub-committee appointed to review the Wages Agreement in the coal mining industry, the Mining Association is of opinion that an authoritative announcement should be made with reference to the attitude taken up by the representatives of the owners on that committee.

It will be remembered that the demands put forward by the Miners' Federation were as follows:—

<sup>4</sup> Munroe, Charles E.: "Chemicals and Allied Products," *Census of Manufactures: 1905, Bulletin 92, Bureau of the Census, Department of Commerce and Labour, Government Printing Office, Washington, 1908.*

1.—That the ratio of profits to wages should be altered from 17 to 100 below the standard and 17 to 83 above the standard to a constant ratio of 13 to 100 both above and below.

2. That the minimum wage should be raised from 20 per cent. to 40 per cent. above the standard.

3.—That further information should be accorded to the miners on costs other than wages.

In the course of the discussions on Thursday last, it was stated by Mr. Evan Williams on behalf of the owners that on certain points the members of the sub-committee had an open mind, and would be prepared to recommend to the members of the Mining Association certain alterations in the Wages Agreement which would operate to the advantage of the men, provided that certain concessions were made by the Miners' Federation in regard to clauses that inflicted undue hardship upon the owners in the less prosperous districts.

As regards the first claim, for the alteration in the ratio between profits and wages, the owners' representatives on the sub-committee were prepared to consider putting forward a recommendation that the ratio should be constant both above and below the standard, and that the proportion allotted to profits should be something less than 17. No precise figure was mentioned, but it was indicated that it would have to be considerably higher than the 13 demanded by the Federation.

As regards the second demand, the owners found themselves unable to make any concession, and it was pointed out by Mr. Evan Williams that the proposed alteration in the minimum from 20 per cent. to 40 per cent. above the standard would not ameliorate the position of the lower paid men, on whose behalf the miners' leaders were putting forward the demand, since these men were already protected by the subsistence wage. For instance, in South Wales the standard wage for surface labourers is 5s. 3.9d. per shift, and the minimum wage therefore is 6s. 4.8d. If the minimum were raised to 40 per cent. above standard, the figure would be 7s. 5.5d., whereas under the subsistence wage it is actually 7s. 6d.

The suggestion was, however, put forward by Mr. Evan Williams that the lot of the lower paid men might be sensibly improved by a redistribution of wages as between them and the higher paid piece workers. He instanced the 14.2 per cent.

advance which was awarded to the piece workers to make up for loss of earnings consequent upon a reduction of the hours from 8 to 7, and suggested that this might be more equitably allocated to the lower paid men.

As a result of this advance of 14.2 per cent., the earnings of the piece workers showed a greater relative increase over their pre-war earnings than did those of the lower paid men, whose need was actually the greater. For the whole of the United Kingdom, except Northumberland and Durham, which were unaffected by the alteration in hours, the percentage increase for the higher paid piece workers was 73, as against 59 for the lower paid men.

As regards costs other than wages, Mr. Evan Williams emphasised that the items for which the miners were asking for further information were such as could not be influenced in any way by them (the miners). At the same time, he said, the representatives of the owners had been favourably considering this demand, and were prepared to recommend that a considerable volume of further information should be given.

The principal counter proposal put forward by the representatives of the owners was in connection with the recoupment of standard profits sacrificed in order to pay the minimum wage which, under the award of the independent chairman, are practically irrecoverable out of any future surplus. The representatives of the miners were reminded that this was not the intention of those who originally drafted the Agreement, and it was indicated that the owners would certainly require the revision of this restrictive interpretation as a *quid pro quo* for any concession that they might be prepared to make. At the same time they realised that to recover out of any immediately ensuing surplus an accumulated deficit might impose considerable hardship on the miners, and they would therefore be prepared to consider proposals for spreading such recoupment over a period occupied by several ascertainment.

In conclusion, the Mining Association wishes to emphasise the point that members of the sub-committee, in putting forward the above-mentioned suggestions for further discussion, were animated by the sincere conviction that the termination of the Wages Agreement at the present time would be a national disaster. It is realised that this Agreement is a far from perfect instrument, but at the same time it is held to be the greatest step forward yet made in

the history of British industry towards settling differences and apportioning the proceeds of an industry between labour, capital, and management. It was these considerations, and not any conviction that the agreement had hitherto operated too much to the advantage of the owners—who indeed have received far less under it than they were entitled to expect—that led the representatives of the owners to make this further attempt to secure for the coal mining industry that peace which is so essential to national recovery.

It is upon the ability of the industry to pay that the owners take their stand. The demand for an increase in the minimum to 40 per cent. above the standard destroys the whole spirit of the Wages Agreement, which was based fundamentally upon the conception that the industry must henceforward be self-supporting and must pay its own way. If the demand were conceded, the wages in the poorer districts would no longer rest upon the ability to pay, and this would render impossible any form of national agreement. Any artificial increase in the price of coal would be merely an effort to bolster up an uneconomic situation, and would break down in practice after having caused a great increase in the volume of unemployment.

It was pointed out to the representatives of the miners that in the poorer districts the rate of output showed a greater reduction per person employed than in the more prosperous areas. The solution of the problems facing the coal industry can only be found by an increase in output per person, and it is extremely doubtful whether such increase can be achieved, at any rate in the poorer districts, under the present restrictions—embodied in an Act of Parliament—on the number of hours worked underground.

## FEDERATION OF BRITISH INDUSTRIES.

(Incorporated by Royal Charter.)

### REPORT OF THE COMMITTEE ON CENTRAL AND LOCAL TAXATION.

The Committee was appointed by the Executive Committee in February, 1923, with wide terms of reference, to consider the whole question of central and local taxation and administration, particularly in

regard to the desirability of decentralisation of control and of greater industrial representation on local authorities. The following Report of the Committee was adopted by the Executive Committee of the Federation on December 12, 1923:—

#### BURDEN OF TAXATION UPON INDUSTRY.

The Committee feel that there is no need for them to dwell upon the burden which is being borne by industry in the form of taxation at the present time. Of the huge amount levied annually for the national exchequer, by far the largest portion is derived in one form or another from industrial sources. To this burden must be added the further contribution which has to be made by industry in the form of rates. The growth of municipal expenditure in the course of the last twenty years has been extraordinary, and although the most recently published figures show that some reduction is now beginning to be effected, the total still remains at a very high figure.

A further fact which intensifies the burden is the unfair inclusion of machinery for rating purposes. This accentuates the inequalities as between industrialists and other ratepayers. The Committee understand that the Government has appointed a Committee to investigate this question, and the publication of a Draft Rating and Valuation Bill is evidence that the whole question of assessments is receiving consideration. The Committee consider that legislation on the question of machinery rating in England is urgently required, and strongly recommend that the Federation should carefully examine the question by means of an expert Committee, with a view to giving evidence before the Departmental Committee.

#### INCREASE IN RATES SINCE 1913.

The Committee have recently made enquiries from firms in a great variety of industries and scattered throughout the country, with a view to comparing the amounts paid by such firms to local rates in 1913 and 1922. The result of their enquiry shows that the payments to rates increased on an average no less than 295 per cent. in the period mentioned, in spite of the fact that contributions to health and unemployment insurance, which might have been expected to reduce the contribution to poor relief, have actually increased 328 per cent. Making all allowances for the difference in conditions between the two years mentioned, and in certain cases the increase in assess-

ments due to extensions of works, the Committee still feel that so large an increase is unjustifiable. When these percentage increases are compared with the increase in the cost of living, which, according to the index figures, rose from 100 in 1914 to an average of 181.5 in 1922, or the increase in the index of wholesale commodity prices from 100 in 1923 to an average of 159 in 1922, it is clear that *prima facie* evidence of the necessity for an enquiry into the whole system is afforded.

#### INCREASED COST OF LOCAL GOVERNMENT SINCE 1913.

The Committee are aware that the cost of local government must be higher at the present time than before the war. The increased cost of living is reflected in higher wages and greater cost of materials, while the trade depression has been responsible for a large increase in the cost of relieving distress. Many expenses which normally would have been carried out during the war years have been postponed, and, in addition, new services have been imposed upon local authorities as the result of legislation passed since 1913. Tuberculosis, venereal diseases, maternity and child welfare, and mental deficiency services have all been added to the duties of local authorities since that date. There are also increased charges in connection with housing and with the registration of electors under the Representation of the People Act.

The Committee do not wish for a moment to suggest that the objects of this expenditure are not from a social point of view eminently desirable. They believe, however, that largely owing to the unsatisfactory demarcation of functions between the central and local authorities, the administration has not been upon the most economical basis, and that the results obtained have hardly been commensurate with the expenditure involved.

#### LOCAL EXPENDITURE AND CENTRAL CONTROL.

Many of these services are financed partly by contributions from State Funds, and the Central Government Department dictates to the local authority the expenditure which must be incurred. In all cases, although the administration is carried out locally, a greater or lesser degree of control is retained in the hands of the Central Government Department. The Committee are convinced that this must inevitably, and in practice does, result in overlapping and extravagance of administration. This arises not merely from the duplication of inspec-

tion, which takes place notably in connection with the administration of the Education Acts, but also from the fact that Parliament and the Treasury are less well placed to exercise detailed control over the minutiae of local expenditure than the local ratepayers, to whom the members of the administrative committees are directly responsible.

#### RELIEF OF DISTRESS.

A very striking example where there is probably overlapping in expenditure as well as in administration is afforded by the payments for relief of distress and unemployment. It is particularly unfortunate that these result in swollen rates at a time when industry is least able to bear an additional burden. The effect of this was shown in 1922 in the case of one distressed area where the poor rate per ton of steel manufactured (comparing the output for the respective years) had increased no less than 2,396 per cent. since before the war, an increase in the cost of production which, of itself, would have no small effect in restricting the flow of orders and thus indirectly causing unemployment.

While it is difficult to form any estimate of the extent to which there is overlapping of relief from the different sources, the Committee would call attention to the lack of co-ordination at present existing in the administration. Unemployment payments, poor law relief,\* feeding of school children, are all directed towards the assistance of the same class of beneficiaries, and the fact that the administration of these services has not been co-ordinated cannot fail to have resulted in extravagance. This matter was dealt with at some length in the report which was presented to the Grand Council a year ago by the Unemployment Insurance Committee.

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\* NOTE.—A further point with regard to poor relief is that in recent years the Ministry of Health has given permission to Boards of Guardians to raise short-term loans from private lenders, amounting in some cases to very large sums. While it may have been inevitable that extraordinary additional sums should be raised for the relief of distress, it is, in the opinion of the Committee, most undesirable that the money should be raised in this way to meet current expenditure, and that borrowing powers of this nature should be conferred upon Boards of Guardians.

The Committee would call attention to the valuable suggestions which have been made on this subject by the Denison House Committee on Public Assistance. That Committee has advocated the publication of a complete and up-to-date annual return of all expenditure from rates and taxes on direct public assistance, with details as to administrative cost, and, further, of a register of beneficiaries, which they maintain must be the basis of all reform. The Committee strongly commend these proposals, and further support the adoption of the Denison House Committee's recommendation of an annual estimate of future public expenditure on direct public assistance, as soon as general conditions become sufficiently normal to make this practicable. The Committee are convinced of the economies which can be effected by a greater co-ordination of public assistance.

#### NEED FOR RECONSIDERATION OF DUTIES OF LOCAL AUTHORITIES.

In view of what is said above, the Committee feel that the time has come to reconsider the duties of local authorities and the scope of the functions which should be delegated to them. Not only should the Central Government take as much advantage as possible of local patriotism and local talent; it should also allow greater autonomy in administration to local authorities within the zone of approved expenditure, and although the need will remain for financial assistance to be afforded by the national exchequer, this, when approved, should not be accompanied by the detailed control at present exercised by the Central Departments. The Committee agree that some safeguards will be necessary, and they would suggest for consideration that where, after a public enquiry held by the Ministry of Health, it is shown that a local administration has been guilty of extravagance and abuse of the powers vested in it, the Ministry of Health should be empowered to suspend the local authority concerned, and to appoint directly stipendiary administrators to carry out its duties.

#### "ONEROUS" AND "BENEFICIAL" SERVICES.

The Committee wish to qualify their suggestions for a reconsideration of the functions of local authorities by referring to the distinction which has been drawn by the Royal Commission on Local Government in 1896 and the Departmental Committee, which reported in 1914, between "onerous" and "beneficial" services. "Onerous" services are defined as those which a local

authority is called upon to perform for the benefit of a greater area than its own locality, while "beneficial" services are those which confer a merely local advantage. They consider that this distinction should be kept in mind, although conditions have changed so much since the Report of the Departmental Committee was issued that the conclusions now reached would probably differ in some respects from those of that Committee.

#### NEED FOR COMMITTEE OR COMMISSION ON INCIDENCE OF TAXATION.

Before, however, any final recommendations can be made on this subject, a strong Committee or Commission should be appointed to examine the incidence of taxation. At the present time the exact incidence of contributions to national or municipal exchequers is to a great extent a matter of guesswork, though both classes of taxation undoubtedly add to the cost of production. The Committee feel that it is a matter of the greatest importance that an enquiry into this subject should be initiated without delay.

The Committee have already called attention to the Draft Rating and Valuation Bill which is now receiving the attention of authorities interested throughout the country. They understand that detailed recommendations in regard to this Bill are being considered by the Taxation Committee of the Federation, and they therefore do not propose to go into its provisions. They regret, however, that the Government have decided to bring forward this Bill before they have initiated an enquiry into the incidence of taxation. For the same reason they are not satisfied that the investigations at present being carried out by a Royal Commission into the question of the areas of local government and by a Departmental Committee into the percentage grant system can adequately meet the difficulties of the situation, and while they do not doubt that both these enquiries will result in useful information being obtained, they feel that the problem has more fundamental aspects than can be dealt with under the terms of reference of either body. For these reasons they recommend that a Committee or Commission should be appointed, with the terms of reference which they have indicated.

#### TRADING SERVICES.

Before concluding their Report, the Committee desire to record that they are not able to suggest any fresh resources which



can be drawn upon to meet local expenditure. In more prosperous times the trading services carried out by municipalities could be ranked as assets, since their operations resulted in profits which went to relieve the rates. Now, however, this position has been reversed, and these services are in many cases a definite liability leading to substantial increases in already heavy rates. Thus, in the case of one local authority, whose budget they have had an opportunity of considering, the Committee note that for the year 1913-14 trading services showed a credit balance of £91,600. In the year 1922-23 this has been converted into a debit balance of £118,323. This new situation requires a complete review of the principle of municipal trading services. The Committee are convinced that the principle should be generally adopted that trading services must be self-supporting, and, if not, should be discontinued in favour of private enterprise. By this they do not mean that each year's working must show a profit, but they consider that if over a period of years a trading service shows a loss, power should be taken to close down that particular trading activity, and thus relieve the rates from the necessity of subsidising it. Moreover, the Committee consider it wrong in principle that profit should be the primary object for which municipal enterprises are instituted. Such enterprises should be judged entirely on the ground of public policy involving such questions as the anticipated service to the community, the dangerous effect of political pressure on costs and charges, and the probable influence upon the competitive and other industries. As to other possible bases of taxation besides that which at present supports the rating system, the Committee find themselves in agreement with the Royal Commission on Local Government and the Departmental Committee that no suitable further local taxes can be imposed.

#### REPRESENTATION ON LOCAL AUTHORITIES.

The Committee regret to record the general apathy of industrialists, which has prevented them from serving on local authorities or encouraging their staffs to do so. They are glad to note that in certain parts of the country a greater interest in municipal affairs is being taken by industrialists, and trust that this movement will spread. They cannot but feel that the experience of business men should be of the greatest advantage in municipal work, and that much

extravagance in the past can be traced to the ignorance of business principles shown by the administrators. The Committee do not wish to suggest that industrialists or the staffs of industrial firms should serve upon local authorities as delegates of industrial interests or in any other capacity than as citizens, but they desire to record their conviction that heads of firms who will themselves serve upon municipal councils or will encourage suitable members of their staffs to do so will be performing a public service of the greatest importance.

#### ARGENTINA—EXHIBITION OF EDUCATIONAL MATERIALS.

The Department of Overseas Trade is informed by the British Legation at Buenos Aires that the American Academy of History (President, N. Sarmiento) is organising an International Congress of History and Geography of America and Exhibition of Educational Materials, to be held in Buenos Aires in 1924.

The Academy invites all scientific and geographical institutions to participate, as well as manufacturers of and dealers in materials concerned in the supply of educational institutions, libraries, science laboratories, etc.

If the project is of interest to United Kingdom institutions or firms, further particulars of the scheme may be obtained from the Secretary of the Academy, Dr. A. E. de la Guardia, Academia Americana de la Historia, Buenos Aires.

#### PROCEEDINGS AND NOTICES OF SOCIETIES.

##### THE CHEMICAL SOCIETY.

Papers read at the Ordinary Meeting on December 20:—

*The Relation between the Glow of Phosphorus and the Formation of Ozone*, by W. E. DOWNEY.

The amount of ozone produced in the slow oxidation of phosphorus was shown to be proportional to the intensity of the glow. Oxygen was led at varying pressures over phosphorus, the oxides of phosphorus formed were frozen out, and the ozone was absorbed in a solution of potassium iodide. The intensity of the glow was measured

photographically. The light of the glow, after passing through a quartz or fluorite window, was shown to ozonise oxygen. The oxidation of phosphorus trioxide was accompanied by the formation of ozone; and the glow was also capable of ozonising oxygen. The glow was shown to be capable of ionising air, and must therefore contain light of the region  $\lambda = 1200-1800$  A.U. The fact that the glow extends into this region gives a possible explanation of the formation of ozone and ions found in the presence of glowing phosphorus.

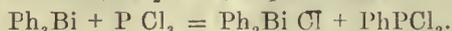
*The Origin of Mutarotation and the Mechanism of Isomeric Change. A Reply to Baker, Ingold, and Thorpe*, by T. M. LOWRY.

The view that water does not intervene in the mutarotation of sugars was criticised on the grounds that it is not in accordance with experimental data, and that the method of proof based upon the form of the mutarotation curves was not valid.

*The Action of Inorganic Haloids on Organo-Metallic Compounds*, by F. CHALLENGER and F. PRITCHARD.

The interaction of the triphenyl derivatives of phosphorus, arsenic, antimony and bismuth with the corresponding trihaloids in ethereal solution has been studied at ordinary or slightly elevated temperatures, to determine whether the reactions largely depended on solubility factors, or if definite rules could be discovered which govern the migration of phenyl groups from one element to another.

With triphenylbismuthine and various haloids, sparingly soluble diphenylchlorobismuthine,  $\text{Ph}_2\text{BiCl}$ , is produced:



Similar results were observed by Goddard and others, with the tetraphenyl derivatives of tin and lead.

A similar, though weaker, tendency is observed with triphenylarsine, though partly obscured by the formation of additive products. Thus, with antimony trichloride, some phenyldichloroarsine,  $\text{PhAsCl}_2$ , is produced, and also an additive product giving the arsine and antimony oxychloride with water.

With triphenylphosphine the tendency for migration of the phenyl group has almost disappeared, additive products always resulting. These undergo an interesting decomposition on heating, giving rise

to the free metal, and presumably, to  $\text{Ph}_3\text{PCl}_2$ , which, with water, gives triphenylphosphine oxide,  $\text{Ph}_3\text{PO}$ . This holds for the haloids of phosphorus, arsenic, and bismuth, and, to a much smaller extent, of antimony, no phosphine oxide being isolated in this case. Phosphorus trichloride is only reduced to a subchloride. When triphenylstibine interacts with metallic haloids these are also reduced and triphenylstibine dichloride formed. Migration of the phenyl group occurs but rarely.

The difference in the behaviour of the phosphine and stibine from that of triphenylbismuthine may possibly be explained on the assumption that the last-named compound is slightly ionised in ether, whereas the others are much less ionised. However, the work of Hevesy and Zechmeister (*Ber.*, 1920, LIII., 410) appears to show that tetraphenyl plumbane,  $\text{PbPh}_4$ , is not ionised in pyridine or amyl alcohol.

*Organo-Derivatives of Bismuth. Part VII.: Iodo- and Nitro-Derivatives of Triphenylbismuthine*, by J. F. WILKINSON and F. CHALLENGER.

Interactions between triphenylbismuthine and iodine and cyanogen haloids have been further investigated. It has been shown that triphenylbismuthine di-iodide,  $(\text{C}_6\text{H}_5)_3\text{BiI}_2$ , exists at low temperatures, but immediately decomposes in ethereal solution at room temperature. At ordinary temperatures, triphenylbismuthine and iodine yield diphenyliodobismuthine and phenyldi-iodobismuthine in varying proportions. Additive compounds of triphenylbismuthine and cyanogen haloids were not formed, the products being diphenylchloro-bismuthine, diphenylbromo-bismuthine, and benzonitrile with cyanogen chloride and bromide respectively, whilst cyanogen iodide yielded diphenyleyanobismuthine and iodobenzene. Cyanogen iodide reacts readily in dry ether with the triphenyl-derivatives of phosphorus, arsenic, and antimony, forming primarily the iococyanides, which immediately decompose with traces of moisture, yielding hydrogen cyanide and the oxide (of triphenylphosphine) and hydroxyiodides (of the triphenyl-derivatives of arsenic and antimony) respectively. Attempts to nitrate triaryl bismuthines, with the object of determining the directing influence of the bismuth atom towards substituents, have failed, benzoyl nitrate giving only the respective bismuthine dinitrates, whilst acid

reagents completely disrupt the molecule with the production of *m*-dinitrobenzene. Derivatives of quinquevalent bismuth, however, are readily nitrated, giving more or less stable meta-nitro-triphenylbismuthine dinitrates, which yield crystalline dihaloids. Of these compounds, the tetra-nitrated derivatives appear the most stable. The dichloride yields the corresponding dihydroxide, a stable compound of a type which hitherto has not been prepared: treatment of this with hot alcohol furnishes a trinitrotriphenylbismuthine.

#### THE ROYAL INSTITUTION OF GREAT BRITAIN.

The subsequent Christmas Juvenile Lectures arranged by the Royal Institution, entitled *Concerning the Nature of Things*, by SIR WILLIAM BRAGG, are as follows:—

II.—Saturday, Dec. 29: *The Nature of Gases*.

III.—Tuesday, Jan. 1: *The Nature of Liquids*.

IV.—Thursday, Jan. 3: *The Nature of Crystals: Diamond*.

V.—Saturday, Jan. 5: *The Nature of Crystals: Ice and Snow*.

VI.—Tuesday, Jan. 8: *The Nature of Crystals: Metals*.

Lecture hour: 3 o'clock.

#### THE INSTITUTION OF ELECTRICAL ENGINEERS.

The Wireless Section will hold a meeting on Wednesday, January 2, at 6 p.m. when a paper entitled *Some Experiments on the Screening of Radio Receiving Apparatus* will be read by R. H. BARFIELD, M.Sc., student.

#### THE ROYAL AGRICULTURAL SOCIETY OF ENGLAND.

The proceedings at the Monthly Council, on Wednesday, December 12 (Lieut.-Col. E. W. Stanyforth, President, in the chair), included, among other matters, the presentation of the following report of the Chemical Committee:—

##### CHEMICAL.

Mr. J. L. Luddington (Chairman) reported that Dr. Voeleker had presented the

list of samples analysed by him during the month of November. The Annual Report of the Consulting Chemist had been considered by the Committee and passed for publication in the next volume of the Journal. The Chairman had reported that he had attended and given evidence before the Departmental Committee on the Fertilisers and Feeding Stuffs Act. Dr. Voeleker had reported on several matters arising out of his correspondence. These dealt with inferior cotton cake, basic slag which was adulterated with ground phosphate, and African phosphate which was insufficiently ground and consequently practically useless. The Leaflet giving particulars of the cases reported at the November meeting of the Committee had been circulated to all the Governors and Members with the report of the Council to the annual general meeting.

The Committee estimated that for the ensuing year their expenditure would amount to £400, plus the amount of the Laboratory petty cash.

The Committee had met eight times and had made eight reports during the year.

#### ELECTROLYTIC PRODUCTION OF ACTIVE HYDROGEN.

BY Y. VENKATARAMAIAH AND BH. S. V. RAGHAVA RAO.

[From the "Journal of the Science Association, Maharajah's College, Vizianagaram.]

Attempts at the preparation of "active hydrogen"—

(i) by the electrolysis of solutions of electrolytes;

(ii) by the action of acids on metals, by Y. Venkataramaiah (*Proc. Sci. Assoc., Maharajah's College, Vizianagaram, July 10, 1921, p. 2*), Wendt and Landauer (*J. A. C. S., Vol. XLIV., No. 3, p. 513*), ended in a failure. Wendt and Landauer describe reasons for their failure thus:

"We are here between two experimental difficulties. The hydrogen must be evolved so rapidly that it reaches the sulphur within a minute, to avoid the decomposition of the active form into the ordinary. On the other hand, if evolution is made rapid, the gas carries with it large amounts of spray which are practically im-

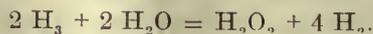
possible to remove without slowing up the stream of gas more than can be allowed. . . Hence the sulphur may well have become coated with a film of moisture which prevented the access of the active hydrogen."

The authors have now repeated the experiments, using a slightly different experimental technique from that of the American chemists, and found the possibility to demonstrate the presence of active hydrogen in electrolysis. Wendt and Landauer have shown (*J. A. C. S.*, Vol. XLII., No. p. 937), that nitrogen combines directly with active hydrogen to form ammonia. Taking advantage of this fact, the authors set up an electrolytic cell with platinum electrodes, one of the electrodes being a small platinum tube of length 30 mm. and of internal diameter 1.0 mm. and external diameter 1.5 mm. It is perforated with a number of pin-holes. A current of 3 to 15 amperes is employed to electrolyse a dilute solution of sulphuric acid. During the course of electrolysis a current of pure nitrogen is sent through the perforated electrode into the solution. The nitrogen combines with the active hydrogen liberated during the course of the electrolysis to form ammonia, and the ammonia is fixed as ammonium sulphate. After a run of about 12 hours the electrolytic liquid, on treatment with alkali, gives unmistakable tests for the presence of ammonia. Similar is the case with caustic potash solution.

To confirm the results obtained above, a second series of experiments is undertaken, in which the permeability of iron to nascent hydrogen at ordinary temperatures is utilised. For this purpose an iron tube 30 cms. long and 12 mm. diameter, closed at one end, is fixed in a tube provided with a nickel electrode and containing water acidulated with sulphuric acid. The iron tube is connected to a glass bulb containing cold powdered sulphur, which in its turn is connected to a small glass bulb packed with glasswool. This again is connected to a small glass bulb containing a lead-acetate paper kept moist by dipping in a solution of the acetate. This bulb is finally connected to a rotating exhaustion pump. During electrolysis the iron tube is made the anode and the pump is kept running. Atomic hydrogen which diffuses through the iron tube yields a little triatomic hydrogen. This combines with sulphur to form hydrogen-sulphide as indicated by the blackening of lead acetate paper in a few hours.

In this connection the authors propose the following simple device for lecture demonstrations, to show the production of triatomic hydrogen during electrolysis. A long glass tube, about 150 cms. long, provided with a small iron cup at one of the ends, is filled with mercury and inverted over a trough of mercury. About 1 cc. of pure nitrogen is then sent into the Torricellian vacuum. Acidulated water is next poured into the cup and the water electrolysed, making the cup the anode. After a time a few ccs. of Nessler's reagent introduced into the vacuum show a distinct brown colouration indicating the presence of ammonia in the tube.

Preliminary experiments conducted show that the failure in the experiments of Wendt and Landauer is to be ascribed not only to the protective coating that the spray forms on sulphur, but also to its distinct chemical action on active hydrogen with the formation of hydrogen peroxide and molecular hydrogen. The reaction may be represented thus:—



*Research Laboratories,  
H.H. The Maharajah's College,  
Vizianagaram.*

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#### CORRESPONDENCE.

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#### COSMISM.

*To the Editors of THE CHEMICAL NEWS.*

SIRS,—Mathematico-physicists as a body, rather than the individual as thinking unit, have decided that the fourth dimension of space is a legitimate conception, and that the space-time velocity of light is the only rigid constant. Nevertheless, time is simply a ratio of macrocosmic and microcosmic inertia; so that space is timeless and Euclidean, and no ethereal substance exists other than the unit of inertia which is the atomic constant of both matter and energy.

The shape of nuclear atoms, having a Proutian unit half that of hydrogen, was published in 1897<sup>1</sup> contemporaneously with the orthodox electrical theory of matter and the quantum theory. A definite relationship between such shape and the combining capacity of carbon nitrogen and oxygen unexpectedly emerged, and was published in 1900<sup>2</sup> and again in 1913<sup>3</sup>.

Torricelli weighed the atmosphere and Boyle measured its elasticity; but such materialistic results were rejected for forty years. The ether likewise can be weighed, its elasticity measured, and its electrons counted. When Sir Ernest Rutherford shattered the atomic nucleus of nitrogen, the real subatomic unit should have been revealed. It had  $\sqrt{2}$  times the velocity of hydrogen, corresponding to a mass unit of one-half, but a crucial experiment is awaited to settle this problem. Likewise, positive ray parabolas with half the normal energy of hydrogen were obtained in 1919, but unwarranted assumptions bolster up the electrical theory of matter.

The identity of ordinary mechanical mass and electrical mass is responsible for much confusion of thought, but an atomic ether solves the problem.

The ether is a perfect atomic fluid, in which the structural loss of an atom forms the Osborne-Reynolds electron, which can be intermolecular only. Atomic numbers represent potential electrons formed endothermically from kinetic electrons by subatomic aggregation at stellar temperature. Planetary gravitational vortices are immutable and indestructible in such perfect fluid. A positive ether pressure ( $0.5 \times 10^{21}$ ) deduced from  $c^2 = p/d$  and  $R^2 = D/d$ , where  $c = 3 \times 10^{10}$ , while  $R = 2.46$  the refractive index, and  $D = 3.5$  the density of diamond, but such should be determined at zero, carries the negative quanta<sup>4</sup> dynamics of electron propagation through the ether struc-

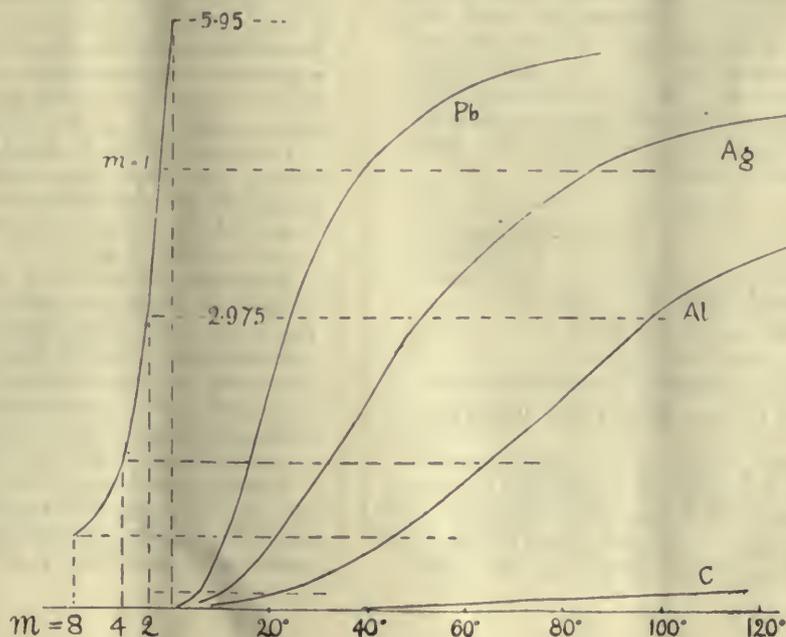
ture by a virtual longitudinal pulse, producing the concentrated photo-electric or photo-chemical effect as a molecular phenomena. The pressure,  $p$ , operates the inverse Osborne-Reynolds electron repulsion, or total inductive capacity, usually denoted by  $K$ , while the magnetic permeability,  $u$ , is identical with the density,  $d$ .

The molecular-heat equation published in 1920<sup>5</sup> is unintelligible to a physicist accustomed to an electrical atom. The simple form of that equation is

$$k = m \log T \quad (1)$$

where  $k$  and  $\alpha$  are constants for any given element or compound at constant volume. The single dependent variable,  $m$ , representing the physical and chemical association, which is the number of atoms or radicles per molecule, dissipates all the mystery associated with chemical force, as an aspect of entropic force, by showing that the number of atoms or radicles per molecule varies as a simple inverse function of the temperature, and that there is a positive entropic force producing condensation, crystallisation, or solidification, on the one hand; and a negative entropic force producing temperature (*and expansion*) on the other.

With mixtures of chemical elements whose combining capacity is a function of atomic shape, catastrophic ejection of electrons is liable to occur corresponding to the change of state whenever the temperature approaches the specific value relative to any



integral value of  $m$ ; but the association  $m$  is a purely physical or bulk effect, and not a chemical attraction within the field of the atom.

The agreement of equation (1) with the Nernst specific heat curves (obtained by inserting the freedom equation of  $m$ , whose graph is given on the left of Fig. 1) proves that temperature is due to molecular vibration only, and that atomic motion at low temperature is not heat. Therefore a kinetic "Stokes" ether of Proutian subatoms, even with an intrinsic pressure greater than that of solids, to carry the infinitely large negative stresses of gravitation, or the infinitesimal light-quanta, is frictionless. It follows that stresses in the rigid subatom are not heat, notwithstanding Lord Kelvin's dictum.

One dyne per square centimetre is a positive or negative ethereal pressure of 300 volts. The intrinsic pressure of all solids at the absolute zero is equal to the ethereal pressure of eighty-billion tons per square inch.

Will chemistry, and especially photochemistry,<sup>6</sup> indefinitely accept Bohr's physical interpretation for fact when chemical forces with physical expansion and contraction are proved by equation (1) to be the entropic pressures of the ether? Van't Hoff took the work obtainable in the evaporation of unit mass as a measure of the chemical affinity, which is thus a function solely of volume, temperature, and atomic mass.

At higher temperatures increasing electrons separate the concomitant molecules and produce a negative ethereal pressure, or voltage, or vapour pressure, which reduces the intrinsic pressure with its molecular surface-tension until, at a specific temperature, the intrinsic pressure becomes identical with the vapour pressure, so that the molecular surface-tension is zero.

Yours, &c.,  
FRED G. EDWARDS.

171, Roundway,  
Waltheof Gardens, N.17.  
November 17, 1917.

References to author's publications:—

- <sup>1</sup> *Spefn. of Letters Patent No. 1999, A.D. 1897.*
- <sup>2</sup> *Chemistry, J. and A. Churchill, 1900.*
- <sup>3</sup> *Eng. Mech., July 18, 1913 (illus.).*
- <sup>4</sup> *Engineering, Nov. 24, 1916 (illus.).*
- <sup>5</sup> *Chem. News, CXX., 277, June 11, 1920.*
- <sup>6</sup> *Chem. News, CXX., 292, June 18, 1920.*

## NOTICES OF BOOKS.

*The Principle of Relativity: A Collection of Original Memoirs on the Special and General Theory of Relativity*, by H. A. LORENTZ, A. EINSTEIN, H. MINKOWSKI and H. WEYL, with a note by A. SOMMERFELD; being translated from the German by W. PERRETT and G. B. JEFFERY. Pp. VIII. + 216. 1923. Messrs. Methuen & Co., Ltd., 36, Essex Street, London, W.C.2. 12s. 6d. net.

Science advances by means of two main conveyances, viz.: the pantechnicon van with a driving mechanism of a highly complex type, and the plain horse and cart that requires no very special skill to manipulate. This book shows the development of the former method, and it is of necessity highly mathematical. The pantechnicon affords a more elegant means of transportation, but it does not necessarily hide worn-out pieces of furniture. The similes are poor, but they will have to suffice.

The readers of these foundation papers, for the most part put into English from the German by the labours of G. B. Jeffery and W. Perrett, will, of course, bear in mind that some developments have been made in the science of relativity since these papers were written; and, as a result, here and there the views expressed require readjustment.

Notwithstanding, all who are able to delve in this highly mathematical subject should possess this work and study the original methods of exposition.

To the average student of physics many statements appear which will be appreciated if he is seriously interested in the subject. Relativity needs no introduction, so we have contented ourselves with a few selections from the text, which will no doubt be seized upon as gems from the classics.

LORENTZ, 1895.—In the Michelson experiment, "a shortening in the direction of motion in the proportion of 1 to  $\sqrt{1-v^2/c^2}$ , in accordance with the formulæ given in the above-mentioned paragraph."—p. 7.

EINSTEIN, 1905.—"So we see that we cannot attach any absolute signification to the concept of simultaneity, but that two events which, viewed from a system of co-ordinates, are simultaneous, can no longer be looked upon as simultaneous events when envisaged from a system which is in motion relatively to that system."—p. 42.

EINSTEIN, 1905.—"The laws by which the states of physical systems alter are independent of the alternative, to which of two systems of co-ordinates, in uniform motion

of parallel translation relatively to each other, these alterations of state are referred (principle of relativity).”—p. 69. We think that this sentence is not crystal clear, as H. G. Wells would doubtless express it.

“The kinetic energy of the body with respect to the [other bodies]  $\xi$ ,  $\eta$ ,  $\zeta$ , diminishes as a result of the emission of light, and the amount of diminution is independent of the properties of the body.”

$$1 \ L$$

Moreover, the difference  $K_0 - K_1 = \frac{1}{2} \frac{L}{c^2} v^2$ .

“From this equation it directly follows that: If a body gives off the energy  $L$  in the form of radiation, its mass diminishes by  $L/c^2$ . The fact that the energy withdrawn from the body becomes energy of radiation evidently makes no difference, so that we are led to the more general conclusion that the mass of a body is a measure of its energy content; if the energy changes by  $L$ , the mass changes in the same sense by  $L/9 \times 10^{20}$ , the energy being measured in ergs, and the mass in grammes.

“It is not impossible that with bodies whose energy content is variable to a high degree (*e.g.*, with radium salts) the theory may be successfully put to the test [see Richardson’s statement given in *The Chemical News*, 1915, Vol. CXII., page 261].—p. 71.

“If the theory corresponds to the facts, radiation conveys inertia between the emitting and absorbing bodies.”

MINKOWSKI, 1908.—This paper contains in its opening paragraph the famous statement about time and space, which we have italicised: “The views of space and time which I wish to lay before you have sprung from the soil of experimental physics, and therein lies their strength. They are radical. Henceforth space by itself, and time by itself, are doomed to fade away into mere shadows, and only a kind of union of the two will preserve an independent reality.”—p. 75.

“I will state at once what is the value of  $c$  with which we shall finally be dealing. It is the velocity of the propagation of light in empty space. To avoid speaking either of space or its emptiness, we may define this magnitude in another way, as the ratio of the electromagnetic to the electrostatic unit of electricity.”—p. 79. Following Minkowski’s paper are Notes thereon by A. Sommerfeld.

EINSTEIN, 1911.—“One result yielded by the theory of relativity is that the inertia

mass of a body increases with the energy it contains; if this increase of energy amounts to  $E$ , the increase in inertia mass is equal to  $E/c^2$ , when  $c$  denotes the velocity of light. Now, is there an increase of gravitating mass corresponding to this increase of inertia mass? If not, then a body would fall in the same gravitational field with varying acceleration according to the energy it contained. That highly satisfactory result of the theory of relativity by which the law of the conservation of mass is merged in the law of the conservation of energy could not be maintained, because it would compel us to abandon the law of the conservation of mass in its old form for inertia mass, and maintain it for gravitational mass.

“But this must be regarded as very improbable. On the other hand, the usual theory of relativity does not provide us with any argument from which to infer that the weight of a body depends on the energy contained in it. But we shall show that our hypothesis of the equivalence of the systems  $K$  and  $K'$  gives us gravitation of energy as a necessary consequence.”—p. 101.

EINSTEIN, 1917.—“The opinion I entertained until recently, as to the limiting conditions to be laid down in spatial infinity, took its stand on the following considerations. In a consistent theory of relativity there can be no inertia relatively to ‘space,’ but only inertia of masses relative to one another. If, therefore, I have a mass a sufficient distance from all other masses in the universe, its inertia must fall to zero. We will try to formulate this condition mathematically.”—p. 180.

WEYL, 1918.—“According to Einstein the phenomena of gravitation must also be placed to the account of geometry, and the laws by which matter affects measurements are no other than the laws of gravitation.”—p. 202.

The reviewer wrote in 1894, as a note against a paragraph on motion in a book published the same year, the following:—“Knowledge is fundamentally relative; even our knowledge of physical facts and, moreover, finite deductions can be made when using infinite postulates, and here again we find the principle of relativity. We cannot get away from it, nor should we attempt to.” It will be seen from a study of this book how vague ideas, such as this example illustrates, have been crystallised into harmonious form by a powerful mathematical treatment.

In conclusion, the publishers are to be

congratulated on the enterprise shown in placing before relativity students such a monumental work.

*Jacob Green, 1790-1841, Chemist*, by E. F. SMITH. Pp. 34. 1923.

Jacob Green was a quiet, persevering, and enthusiastic American scientist, whose retiring nature prevented his name from being as well known as his attainments justified.

Prof. Smith, of the University of Pennsylvania, has now published a little biographical sketch of Green, which should be an inspiration to the young chemists of today.

*The British Journal Photographic Almanac, 1924*, Edited by GEORGE E. BROWN, F.I.C. Pp. 812. London: Henry Greenwood & Co., Ltd., 24, Wellington Street, Strand, W.C. Paper covers, 2s.; bound, 3s.

The B.J. Almanac for 1924 fully maintains the high reputation established by its predecessors.

In addition to the valuable and complete data concerning the various photographic processes and apparatus, it also includes a very practical article by the Editor, entitled, *Using a Hand Camera*, and an epitome of progress in the subject during the year.

This *Epitome of Progress* constitutes a valuable record of the scientific work accomplished by photographers. Whilst no research of outstanding importance has appeared during the past year, it is noteworthy that steady progress has been maintained in the solution of the problems of photography, especially in regard to lenses and in colour photography.

As a reference volume, the B.J. Almanac is replete with such information as tables (which have been revised) of weights and measures, chemical and physical constants, etc. There is also a useful trade directory.

Chemists who are also photographers should find the Almanac indispensable.

#### BOOKS RECEIVED.

*A Course of Laboratory Experiments on Physico-Chemical Principles*, by WILLIAM C. BRAY and WENDELL M. LATIMER. Pp. X. + 120. 1923. The Macmillan Company, New York, U.S.A.

*Dangerous Goods*, by DR. JULES AEBY. Pp. XI. + 319. 2nd Edition. 1922. Messrs. Crosby, Lockwood & Son, 7, Stationers' Hall Court, E.C.4. 30s. net.



This list is specially compiled for *The Chemical News* by Messrs. Rayner & Co., Registered Patent Agents, of 5, Chancery Lane, London, from whom all information relating to Patents, Trade Marks, and Designs can be obtained gratuitously.

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- 29800—Coke, B. E.—Oxidation of naphthalene, etc. Nov. 27.  
 29801—Coke, B. E.—Oxidation of aromatic hydrocarbons. Nov. 27.  
 29972—Mathieson Alkali Works, Inc.—Manufacture of hypochlorites. Nov. 28.  
 29737—Stevenson, W. J.—Manufacture of acetyl cellulose. Nov. 26.  
 30438—Atkinson, R. G.—Apparatus for chemical action under the influence of light. Dec. 4.  
 30726—Guadagni, G.—Manufacture of acids. Dec. 6.  
 30535—Lichtenthaler, F. E.—Process of concentrating aqueous solutions of volatile substances. Dec. 4.  
 30805—Stokes, J. S.—Synthetic resins. Dec. 7.

#### Specifications Published this Week.

- 197632—Naugatuck Chemical Co. — Processes for vulcanising rubber with condensation products of ammonia and aldehydes as accelerators.  
 198379—Chemische Fabrik Auf Actien vorm. E. Schering.—Manufacture of new barbituric acid compounds.  
 203683—Soc. d'Études Chimiques pour l'Industrie.—Process for the manufacturing from cyanamide of manures containing soluble organic nitrogen.  
 207247—Gardner, D., and Taverner, L.—Extraction of iron and of titanium compounds from titanium ores.  
 207267—Paterson, W.—Apparatus for treating liquids with chemical reagents.  
 199743—Guilleminot, P. L.—Sulphonation of fatty substances of animal origin.  
 207476—Soc. of Chemical Industry in Basle.—Manufacture of vat dyestuffs derived from anthraquinone.

#### Abstract Published this Week.

205563—Aluminium chloride, alumina.—Chemische Fabrik Griesheim-Elektron, of 51, Gutleutstrasse, Frankfurt-on-Main, Germany.

*Aluminium chloride; alumina.*—An aluminium chloride solution which may be obtained by treating calcined clay with hydrochloric acid (or with aluminium chloride solution enriched with hydrochloric acid) is evaporated to produce a crystal sludge from which mother liquor is separated. The crystals are washed with hydrochloric acid or first with some of the original solution, and then with pure hydrochloric acid (for instance of 20 per cent. strength), the mother liquor and washings being used to absorb hydrochloric acid arising from the calcination of the crystals to obtain alumina (when such calcination is effected) or from other sources, and used according to their content of iron either for washing the crystals or for treating more clay. When the solutions accumulate too much iron they are evaporated and calcined to produce hydrochloric acid.

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